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SAMPLING AND IDENTIFICATION OF POLLUTANT OILS IN INDUSTRIAL WATERCOURSES

Robert E. Baier, et al

Calspan Corporation

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by

Robert E. Baier, Edward A. Gasiecki,
Richard P. Leonard, and Eugene J. Mack
Cornell Aeronautical Laboratory, Inc.
Calspan Corporation
Buffalo, New York 14221

Project No. 11020 DJG

Project Officer

Richard R. Keppler
Region I
U. S. Environmental Protection Agency
Boston, Mass. 02203

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16. ABSTRACT

A thoroughly documented discussion of methods for sampling and identifying pollutant oils in industrial watercourses is presented. Simple, yet quantitative, methods for retrieval of oil slick specimens are described which are usable on all types of pollutant layers, ranging from near-zero thickness to inches in thickness, irrespective of their degree of weathering, emulsification, or admixture with debris. Techniques which fail in such situations are also described. An analytical scheme for the determination of organic pollutants in industrial waters by chloroform extraction (below pH 8) and carbon tetrochloride extraction (above pH 8) is demonstrated to be superior to more generally used hexane extraction techniques. Numerous examples illustrating the use of gas chromatography and infrared spectroscopy for pollution analysis are presented. Applications of the various analytical methods considered are discussed with specific reference to the correlation of oil slick components with pollutants in industrial outfalls; the evaluation of an inverted siphon sewer as an oil trap; the evaluation of an air barrier as a slick container; the evaluation of surface oil skimmers; and the identification of spilled oils for enforcement actions. The burden of oily pollutants entering and exiting the Buffalo River, and deposited along its shoreline and in its sediments, is estimated for the 1968-1970 period and compared with available data on the river water quality as early as 1964.

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A thoroughly documented discussion of methods for sampling and identifying pollutant oils in industrial watercourses is presented. Simple, yet quantitative, methods for retrieval of oil slick specimens are described which are usable on all types of pollutant layers, ranging from near-zero thickness to inches in thickness, irrespective of their degree of weathering, emulsification, or admixture with debris. Techniques which fail in such situations are also described. An analytical scheme for the determination of organic pollutants in industrial waters by chloroform extraction is demonstrated to be superior to more generally used hexane extraction techniques. Numerous examples illustrating the use of gas chromatography and infrared spectroscopy for pollutant analysis are presented. Applications of the various analytical methods are discussed with specific reference to the correlation of oil slick components with pollutants in industrial outfalls; the evaluation of an inverted siphon sewer as an oil trap; the evaluation of an air barrier as a slick container; the evaluation of surface oil skimmers; and the identification of spilled oils for enforcement actions. The burden of oily pollutants entering and exiting the Buffalo River, and deposited along its shoreline and in its sediments, is estimated for the 1968-1970 period and compared with available data on the River water quality as early as 1964. Appendices describe special sampling and analytical techniques, and provide a commentary on a film showing the use of surface-active "piston films" against oil slicks.

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CONCLUSIONS

The following conclusions are made relevant to the sampling and identification phase of the Buffalo River Program:

1) Because of the very large and demonstrated variability in the distribution of oils in an industrial watercourse, it is unrealistic to expect short period "spot" or "grab" samples to be reliable within a few parts per million.

2) A chloroform extraction technique for analyzing waters of an industrial watercourse is considered to be superior to techniques which use hexane or carbon tetrachloride.

3) Round-the-clock monitoring is needed in both the sewers and on the River to average out the observed variability and to guarantee the catching of the nuisance large spills which are not likely to be found in a spot sampling program.

4) Sampling techniques for surface oils based on the use of screens and skimmers have limited success, because they become totally fouled with weathered oil which congeals to form a tough resistant grease.

5) During the two-year course of this sampling and identification program, there was a large continuing deposition of oily materials and other pollutants at the bottom and along the banks of the Buffalo River.

6) Surface-active piston films are useful for driving oil films from confined areas, condensing and thickening them, and controlling and directing their motion. Such surface-active piston films are also useful for preventing shoreline impaction of wind-driven slicks and for improving the operating efficiencies of skimmers.

7) Our sampling data show that over the 1969-1970 season, there was a net accumulation of at least 5,000 pounds of oil in the Buffalo River per day and that the major sink of this oil was the shoreline and river bottom.

A major benefit of a study of an industrial watercourse can be the formulation of good working relationships among generally independent parties with overlapping interests in the waterway. For example, in the course of this Buffalo River study, continuing cooperative relationships of benefit to the local community, and to the federal need to control water pollution, have been built up among the following parties: Cornell Aeronautical Laboratory, the City of Buffalo Engineering Office, New York State Department of Environmental Conservation, Harbormaster of the City of Buffalo, the Buffalo Sewer Authority, the Great Lakes Laboratory, the U.S. Geological Survey, the EPA Boston Regional Office, the EPA Edison Water Quality Laboratory, and the Naval Research Laboratory in Washington, D.C. With these organizations, there has been the sharing of knowledge, of manpower, of technical facilities, occasional splitting of the analytical load, and development of mutual trust and confidence in one another's capability by analysis of replicate samples. As documented in a further section of this report, we have been able to jointly respond to "troubleshooting" situations where oil spills have occurred and to the need for the prompt retrieval and identification of samples from such spills.

RECOMMENDATIONS

The following recommendations are based on the results of the extensive sampling and analysis effort conducted as part of the overall Buffalo River Program:

1) A hoop method and a prism-dip method described in the SAMPLING section are recommended for collecting surface oil samples. For thick accumulations of surface oil, where a large amount of debris is present, an *in situ* freezing technique is recommended.

2) It is recommended that the area of the Buffalo River at the South Park Bridge be considered for stream oxygenation studies. This area of the River was found to have zero dissolved oxygen, very high oil content, and very little sign of benthic or other life nearly all year around.

3) It is recommended that development proceed on an inexpensive disposable environmental quality sampling kit and an on-site buoy mounted monitor, both based on the internal reflection spectroscopy technique as outlined in Appendix A to this report.

4) It is recommended that long-term cleanup programs for industrial waterways include scavenging of shoreline deposits using environmentally safe surface-active agents coupled with skimming operations.

5) Follow-on research should be undertaken to compare oil slick samples collected by the various methods used in the Buffalo River (rotating drum, *in situ* freezing, screen-dip, surface-active hoop, prism dip) so that decisions can be made as to which method can be best applied in a variety of circumstances.

6) Additional investigations of air barrier influence on the adjacent water chemistry should be undertaken, after a careful preselection of the location of the air barriers to provide maximum data yield from the experiments.

7) Further development of surface chemical agents which act as "piston films" to displace, collect, and concentrate oil slicks is recommended.

INTRODUCTION AND BACKGROUND

Oil pollution has plagued not only coastal areas, but also inland lakes and rivers which are subjected to oil inputs from industries, service stations, and consumers. The inputs from large industries, especially the oil transportation trade, tend to be fairly large and visible and thus subject to policing. Discharges from small local industries and consumers usually enter sewage systems and prove to be a problem in the treatment process. They are occasionally discharged into open water either because of overflow conditions or because the treatment plant is not able to cope with them. These discharges are very difficult to police and it would be useful if they could be detected in sewers in a fashion which would permit identification of the source of the oil discharge. A reasonable number of oil monitors in each city appear to be adequate for this purpose. For example, in the City of Buffalo, it has been estimated that some 60 sensors, strategically placed, could locate most sources.

In May 1968 the City of Buffalo made application to the Federal Water Pollution Control Administration for a Research and Development Grant for preventing and eliminating oil pollution of the Buffalo River under the provisions of the "Clean Water Restoration Act of 1966." On 24 July 1968 the City of Buffalo accepted a Federal Research and Development Grant (WPRD 263-01-68) for $552,895.00, or 75% of eligible costs, whichever is less. Twenty-five percent of the eligible costs have been provided by the City of Buffalo, the Buffalo Sewer Authority, the County of Erie, and the New York State Health Department in the form of either direct cash contributions or in-kind services. On 18 October 1968 a contract was negotiated with Cornell Aeronautical Laboratory, Inc., (now Calspan Corporation) of Buffalo, New York to provide the research, engineering, and development support required for the program (Calspan Corporation is the new name for Cornell Aeronautical Laboratory. Because this report was completed prior to the date of our name change (November 17, 1972) Cornell Aeronautical Laboratory nomenclature has been retained in this report.).

The overall objective of the program was to prevent oil pollution of the Buffalo River. Specific objectives of the program were:

1) To develop, utilize and evaluate equipment and techniques for containing and removing oil in the river, including floating mechanical barriers and pneumatic barriers for preventing the movement of surface oil, oil skimmers, debris booms, and a boat containing oil and debris removal equipment
2) To develop instrumentation for detecting oil in sewers
3) To evaluate means for trapping oil in sewers
4) To devise methods for sampling oil to determine its concentration in the river, and to develop methods for analyzing the collected samples to determine their sources

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Specific aspects of the program are described in detail in four separate topical reports. This topical report covers oil sampling and analysis for spills in watercourses. The other three reports cover the evaluation of a pneumatic barrier for oil containment (Reference 2), the detection of oil in sewers (Reference 3), and the investigation of inverted siphons for trapping oil (Reference 4). The overall program is described in a summary report (Reference 5).

PLAN OF THE REPORT

The sampling and identification task of the Buffalo River Project had a two-fold purpose: first, to develop reliable sampling techniques and identification methods for oily pollutants in an industrial watercourse, which might be generally useful in similar watercourses across the nation; second, to develop a sufficiently detailed understanding and characterization of the Buffalo River itself to allow measurement of the effectiveness of eventual abatement and clean-up of the gross oil pollution noted there.

In this introductory section, we highlight immediately certain variations and uncertainties in the data collections that were noted during the course of our intensive two-year sampling and identification program. It is believed that these variations are almost certain to be noted in any other industrial waterway to which the technology presented here might be translated, and an explanation of the differences to be expected is of value. As will be documented in later sections, variations occurred in the measured oil content of water samples taken from spot to spot, from time to time, from day to day, and analyzed by methods varying from one to the other and laboratory to laboratory. With these constraints, attempts to enforce effluent or stream quality by reference to the oil content to the nearest part-per-million cannot succeed.

This report has been designed to be self-contained; it is a technical document, complete in itself, on the subject of oil sampling. Thus, it contains some introductory material which may be common to other topical reports on the Buffalo River Project. Also, it is expected that certain specific sections of this report which address other specific tasks, such as analysis of the inverted siphon sewer, analysis of the oil content in the water adjacent to the air barrier, analysis of certain of the oils used in checking skimmer operation, will appear as Appendices to the other topical reports. Throughout, emphasis is placed on those areas of this work which can be extrapolated to other situations where sampling and identification and precise analysis of oily pollutants in and on water are necessary and desirable.

HISTORY AND HYDROLOGY OF THE BUFFALO RIVER

The definition of the Buffalo River that is employed by the United States Geological Survey is adopted here: the Buffalo River is "that stream which is formed by the confluence of Buffalo and Cayuga Creeks." Within the approximately 450 square mile drainage basin of the Buffalo

River, there are known to be over 30 separate tributaries. The Buffalo River has recently become the subject of a large "improvement project" and also target of attempts to monitor the effectiveness of pollution abatement programs by many of the communities now discharging wastes into this stream. The "improvement project" is a cooperative venture involving primarily the City of Buffalo and four of the major industries along the River (Allied Chemical, Donner-Hanna Coke, Mobil Oil and Republic Steel).

The Buffalo River was originally a very narrow, shallow stream. It was estimated that, prior to 1800, the River was never wider than 15 meters nor deeper than 2 meters, even at its mouth at Lake Erie. In the early 1800s, work was done at the mouth of the River to relocate a sand bar and, through the construction of piers, the erosion capacity of the spring run-off was allowed to cut a channel approximately 30 meters wide and 3 meters deep which extended upstream from the mouth at Lake Erie for a distance of approximately 1600 meters. Upon completion of the Erie Barge Canal in 1825, additional dredging of the Buffalo River was undertaken to produce a water depth of 4 meters, and then continued dredging gradually increased this to a depth of 7 meters in stages through the 1800s and early 1900s. The widening and deepening of the channel, plus some alterations which occurred in the natural watershed, decreased the flow rate of the River substantially. Under the stagnant conditions that often then prevailed, the heated water discharged by industry was constantly recycled through the industries themselves and the closed-loop thereby produced often resulted in surface temperatures in the Buffalo River in excess of 90°F.

The portion of the Buffalo River which received major attention in this program begins at the mouth of the River and extends upstream approximately 6 miles to just above the confluence of the Buffalo River with Cazenovia Creek, a major tributary. A schematic plan view of the River to its junction with Lake Erie is given in Figure 1. Industries along the upper reaches of the River include an oil refinery, a steel mill, a large chemical manufacturing facility, and a coke plant. The lower half of the River has predominantly grain storage and milling facilities along its shores. The River continues to be dredged regularly as a Federal project by the Corps of Engineers. The current average River width is 275 feet and the average channel depth is about 25 feet at mean water level.

The hydraulic properties of the River change quite drastically over very short periods of time and over the yearly cycle. In winter, the River and its tributaries from the beginning at Cazenovia Creek to the headwaters are completely frozen over. Ice is present as skim and chunk material in the remainder of the River all the way to the mouth. The sum of the mean annual peak flows (which usually occur in spring) for the tributaries reaches about 22,000 cubic feet/second producing currents of about 3 feet/second near the mouth. After the peak runoff in the spring, the river becomes quiescent and indeed often appears stagnant. The most recent 30-year-average annual flow of the Buffalo River is less than 500 cubic feet/second.

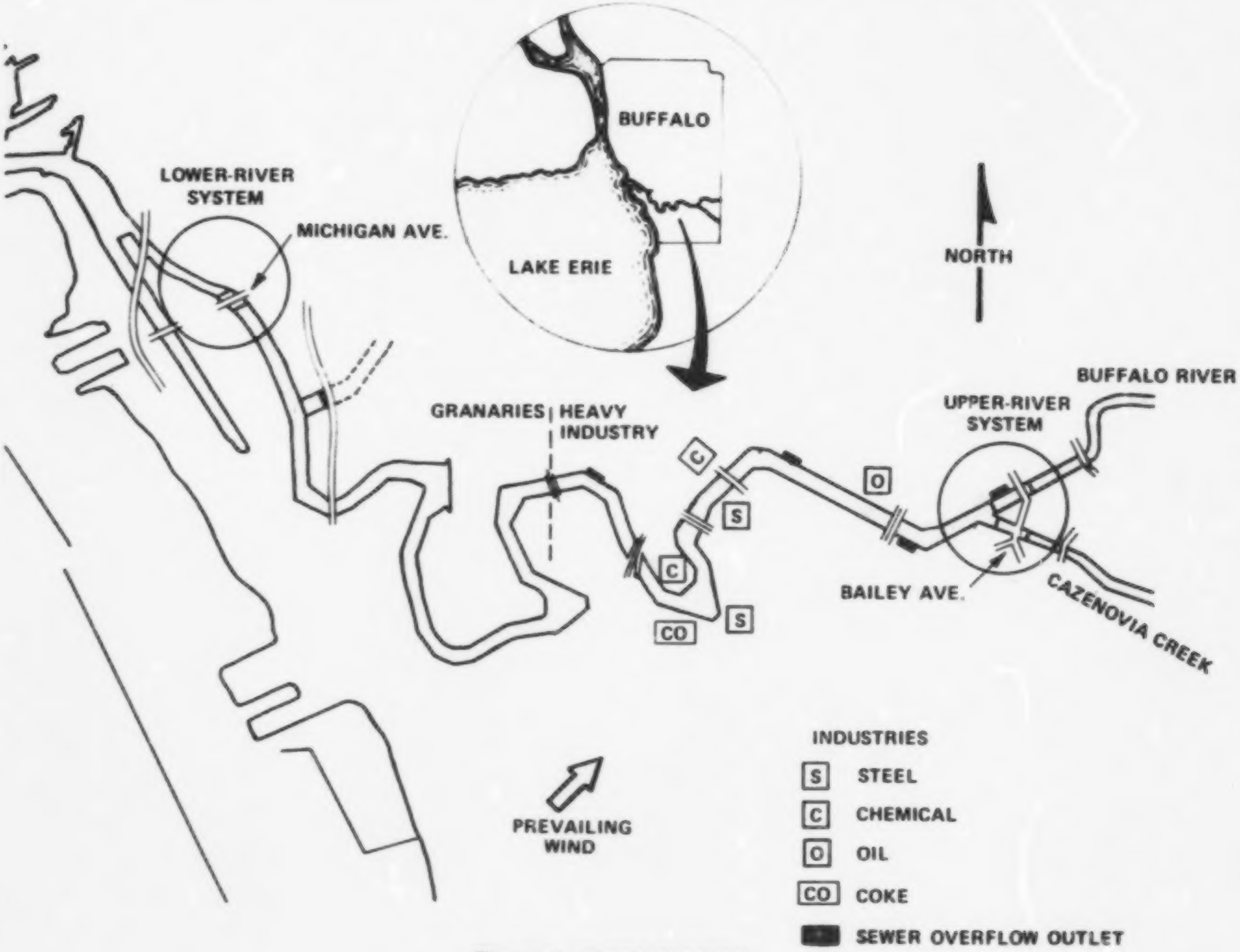
LOWER-RIVER SYSTEM
MICHIGAN AVE.
BUFFALO
LAKE ERIE
NORTH
GRANARIES
HEAVY INDUSTRY
BUFFALO RIVER
UPPER-RIVER SYSTEM
BAILEY AVE.
CAZENOVIA CREEK
C
S
C
CO
S
O
PREVAILING WIND
INDUSTRIES
S STEEL
C CHEMICAL
O OIL
CO COKE
SEWER OVERFLOW OUTLET

Figure 1 MAP OF AREA

During the complete spring, summer and fall seasons of the year, oil slicks are present over most of the River surface. In the spring, it is frequently noted that the oil slicks are more abundant in the lower River reaches, perhaps as a result of scouring of the bottom muds and shorelines and release of the buildup of oil pollution from the melting ice. Throughout the year, the prevailing southwest winds entrap the surface oil and the other pollutant slicks in the upper river reaches, and indeed drive such oil into residential areas beyond the confluence of the Buffalo River and Cazenovia Creek.

EXTENT OF THE OIL POLLUTION PROBLEM IN THE BUFFALO RIVER

The amount of oil discharged daily from industrial sources along the Buffalo River may have diminished slightly over the last two or three years, but as of 1968, when the International Joint Commission issued its comprehensive report on Lake Erie and the major streams which empty into it, it was estimated that some 12,000 lbs of oil each day were being released into the Buffalo River. As a result of our sampling and identification program over the course of the last two years, we can only account for discharge of approximately 7,000 lbs of oil each day at the River mouth in Lake Erie. Therefore, our conservative estimate is that some 5,000 lbs of oil per day are being deposited in the Buffalo River bottom sediments and along the shoreline rocks and commercial structures. In addition, much of the oil released into the industrial sector is carried upstream by the prevailing winds and fluctuations in Lake levels, and is very likely subject to biological degradation in the upper river reaches.

We, as most other water pollution researchers, were most interested in developing reliable knowledge on the circulation and flow of pollutant oils in such an industrial river, and in examining the problem of pollutant dispersion. In all earlier studies, to our knowledge, data have been taken over a very short period, often within a few hours or at the most averaged over a single day or a week. Depending upon which week observations are made in industrial waters, and in particular, in the Buffalo River, drastic differences in direction and magnitude of the flow can be observed, including the case of zero net flow. Lacking a comprehensive collection of data, advice to those who must control pollution in such a situation must be offered with strong reservations. Against the background of data taken over a very long period, as accumulated in this project, short-term observations lose significance. The value of obtaining long series of measurements prior to pollution abatement applications, therefore, is demonstrated. It has also been observed in the Buffalo River that substantial changes in the water quality occur abruptly. Flow changes due to storms are short and unpredictable. Special situations, like shutdowns of major industries because of holidays and strikes, led to unpredictable rates and quantities of oil in the industrial discharges or in occasional spills. Various attempts to trap oils with air barriers and mechanical barriers caused flow changes near these impoundments. All of these variations altered the concentration of the oils and pollutants of most interest to the water pollution abatement specialist.

THE OIL SAMPLING, IDENTIFICATION, AND ANALYSIS EFFORT

The federal grant for research and development which funded this particular program was awarded in July 1968 to the City of Buffalo. In the fall of 1968, a subcontract with Cornell Aeronautical Laboratory, Inc. was negotiated, and a brief sampling series in the late fall of 1968 was accomplished on the Buffalo River before the winter freeze set in. A major sampling and identification program was begun in June of 1969. Since the early program emphasis was placed on booms, skimmers and air barrier evaluation, very little actual analysis of the bulk river water and of the distribution of the pollutant oils was attempted. The bulk water sample analysis over the summer of 1969 was based on a single solvent-extraction technique which more careful work in the subsequent year demonstrated to be inadequate, as documented in a later section. One very important aspect of the high-yield sampling and identification program, however, was that of surface sampling of the publicly apparent oil slicks and the correlation of the materials in those slicks with the source materials entering the Buffalo River at various industrial outfalls.

In 1970, regular sample collection began in April and terminated in October and provided an extensive, careful series of measurements upon which the major conclusions of this report are based. Nearly 50 specific industrial outfall samples and hundreds of river water specimens were collected and analyzed by transmission infrared spectroscopy, internal reflection infrared spectroscopy, ultraviolet/visible spectrophotometry, and gas chromatography, in addition to having analyses made of the total solids content, the pH levels, and other more obvious characteristics, such as color. Also during the 1970 season, chronic problems in determining the actual volumetric consequences of the oil concentrations that were measured, and also problems in proper data reduction, were overcome: namely, the basic unavailability of timely flow data for the river itself. During the 1970 season, through the courtesy and cooperation of personnel of the United States Geological Survey and the Buffalo Sewer Authority, we obtained access to the gauging stations for the feedstreams to the river and to the rating tables for the augmented flow along the river from the cooling water "improvement project." We were thus able to investigate directly the correlation between measured oil concentration and volume of inflow waters from the tributaries and the cooling water project.

In summary, the oil sampling, identification, and analysis phase of the Buffalo River project led to the following results.

1. Sampling. Efficient techniques were formulated for determining via statistically significant samples of appropriate size, the quantity and distribution of oil in emulsified form (that is, in the bulk water), trapped at the bottom (that is, in the sediment) and on the surface (that is, floating in apparent oil slicks) of the Buffalo River.

2. Identification. Standard analytical techniques and new analytical instrumental approaches were developed which were used to identify oily pollutants by their sources. Numerous oil samples were taken in the River, from the various industrial outfalls, and in the City of Buffalo sewer lines which can overflow into the River.
3. Analysis. Information obtained in the sampling and identification tasks was analyzed to evaluate the oil trapping mechanisms in the River and to evaluate the effectiveness of the oil trapping mechanisms in the inverted siphon sewer and during skimming operations.

QUALITATIVE AND QUANTITATIVE ASPECTS OF THE DATA PRESENTED IN THE BODY OF THIS REPORT

As noted earlier, during the course of this investigation significant variations were observed in the analyses of Buffalo River water samples taken from spot to spot within the river, from time to time at a given spot, from day to day at a given spot and analyzed by different methods in the two different chemical laboratories (at the Cornell Aeronautical Laboratory, Inc. and the Buffalo Sewer Authority) which were the prime analytical sites during this investigation. Within each given chemistry laboratory, the maximum variation in oil analysis was found to be ±0.3 parts/million. However, between laboratories having opposite halves of the same shaken, mixed samples, it was occasionally found that the quantitative difference ranged up to a factor of 2. This latter difference reflects unexplained, but nonetheless common, minor differences in sample handling among various laboratory personnel.

Table 1 provides illustrative comparisons of laboratory results of analyses of identical samples of the Buffalo River water by the Cornell Aeronautical Laboratory and by the Buffalo Sewer Authority using a common method, selected and certified by Cornell Aeronautical Laboratory scientists and documented in an appendix to this report. Although this variation is significant and disconcerting by itself, it is superimposed upon a variation that occurs in the quality of the River even within an hour at the same sampling site. Figure 2 is a map which labels the sampling sites which were chosen for the Buffalo River sampling program and which were selectively sampled at various depths from the surface all the way down to the bottom sediments on various dates.

Table 2 chronicles the variation in the oil concentration on one day at four of these sites, Sites 5, 6, 8 and 10 (see Figure 2 for location of sites). It will be noted that there is at least as great a variability over the course of a few hours at any given site as could be accounted for by errors in analysis at any given laboratory. To further compound the problem, not only were there differences from time to time in any given day and from day to day at any given week, but, following a standard routine sampling procedure, it was observed early in the 1970 sampling season that there was a substantial variability in the amount

Table 1
ILLUSTRATIVE COMPARISONS OF LABORATORY RESULTS FROM ANALYSES OF IDENTICAL SAMPLES OF BUFFALO RIVER WATER

SAMPLE	PPM OF CHLOROFORM-EXTRACTABLE MATTER	
	CORNELL AERONAUTICAL LABORATORY	BUFFALO SEWER AUTHORITY
1	1.2	1.3
2	1.6	3.4
3	<1.0	3.0
4	1.6	3.5
5	3.1	1.5
6	4.3	3.0
7	6.8	4.6
8	8.8	4.1
9	1.8	2.3

of oil (determined as chloroform-extractable matter according to a preferred procedure outlined later) in both the surface waters of the Buffalo River and in the bottom waters. Figure 3 charts the weekly variation in chloroform-extractable matter from the surface water of the Buffalo River over a 12-week period. Figure 4 chronicles a similar variation in the chloroform-extractable matter in the bottom water of the Buffalo River over the similar period.

It is also to be understood that when the word "oil" or even the more specific term, "chloroform-extractable material," is used throughout this report, it does not define a specific kind of oil associated with the various levels of the River. Figure 5 is a collection of typical infrared "fingerprints" of oil found, (a) floating upon, (b) suspended in and (c) at the bottom of, the Buffalo River. It will be noted from an inspection of Trace A of Figure 5 that the typical fresh oil slicks often found on the Buffalo River surface have an infrared "fingerprint" dominated by only three major peaks, all of which are typical of petroleum oils, saturated hydrocarbons predominantly, with very little evidence of oxidation. In extreme contrast, Trace B in Figure 5 shows that the infrared "fingerprint" of the organic matter emulsified in the bulk water, in addition to containing an abundant amount of hydrocarbon components, indicates the presence of a substantial amount of oxidized hydrocarbon and esterified material. This is especially well indicated by the ester band in such spectra at about 5.75 microns. Trace C in Figure 5 illustrates a typical infrared "fingerprint" for the organic material which is trapped abundantly in the bottom sediment in the Buffalo River. It should be noted there, as well, that a very large quantity of oxidized and weathered material, as well as straight petroleum oil, is present.

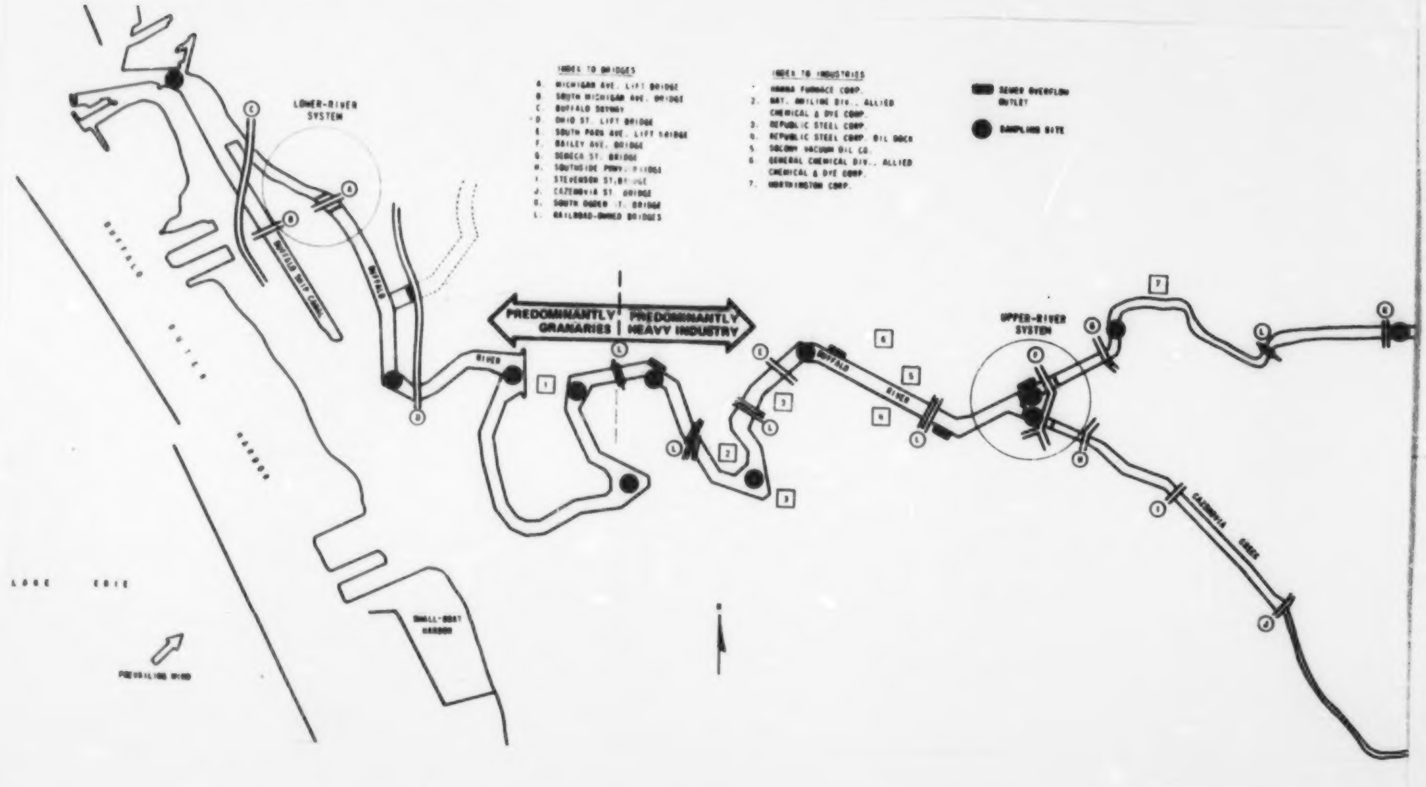
INDEX TO BRIDGES
A. MICHIGAN AVE. LIFT BRIDGE
B. SOUTH MICHIGAN AVE. BRIDGE
C. BUFFALO SKYWAY
D. OHIO ST. LIFT BRIDGE
E. SOUTH PARK AVE. LIFT BRIDGE
F. BAILEY AVE. BRIDGE
G. SENECA ST. BRIDGE
H. SOUTHSIDE PKWY. BRIDGE
I. STEVENSON ST. BRIDGE
J. CAZENOVIA ST. BRIDGE
K. SOUTH OGDEN ST. BRIDGE
L. RAILROAD-OWNED BRIDGES
INDEX TO INDUSTRIES
1. HANNA FURNACE CORP.
2. NAT. ANILINE DIV., ALLIED CHEMICAL & DYE CORP.
3. REPUBLIC STEEL CORP.
4. REPUBLIC STEEL CORP. OIL DOCK
5. SOCONY VACUUM OIL CO.
6. GENERAL CHEMICAL DIV., ALLIED CHEMICAL & DYE CORP.
7. WORTHINGTON CORP.
SEWER OVERFLOW OUTLET
SAMPLING SITE
LOWER-RIVER SYSTEM
UPPER-RIVER SYSTEM
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO RIVER
BUFFALO SHIP CANAL
CAZENOVIA CREEK
BUFFALO OUTER HARBOR
SMALL-BOAT HARBOR
LAKE ERIE
PREVAILING WIND
N

Figure 2 CHOICE OF SITES FOR BUFFALO RIVER SAMPLING PROGRAM

Table 2

VARIATION IN OIL CONCENTRATION ON ONE DAY

TIME	SURFACE WATER CONCENTRATION (PPM)	BOTTOM WATER CONCENTRATION (PPM)
SAMPLING SITE 5		
1045	11.6	13.2
1125	17.6	31.2
1310	18.8	15.4
1430	13.4	9.2
SAMPLING SITE 6		
1050	19.6	2.6
1130	14.4	3.5
1300	11.8	< 1.0
1445	< 1.0	3.3
SAMPLING SITE 8		
1110	12.0	< 1.0
1350	< 1.0	NIL
1500	1.1	22.2
SAMPLING SITE 10		
1100	12.0	< 1.0
1145	10.4	< 1.0
1400	13.0	NIL

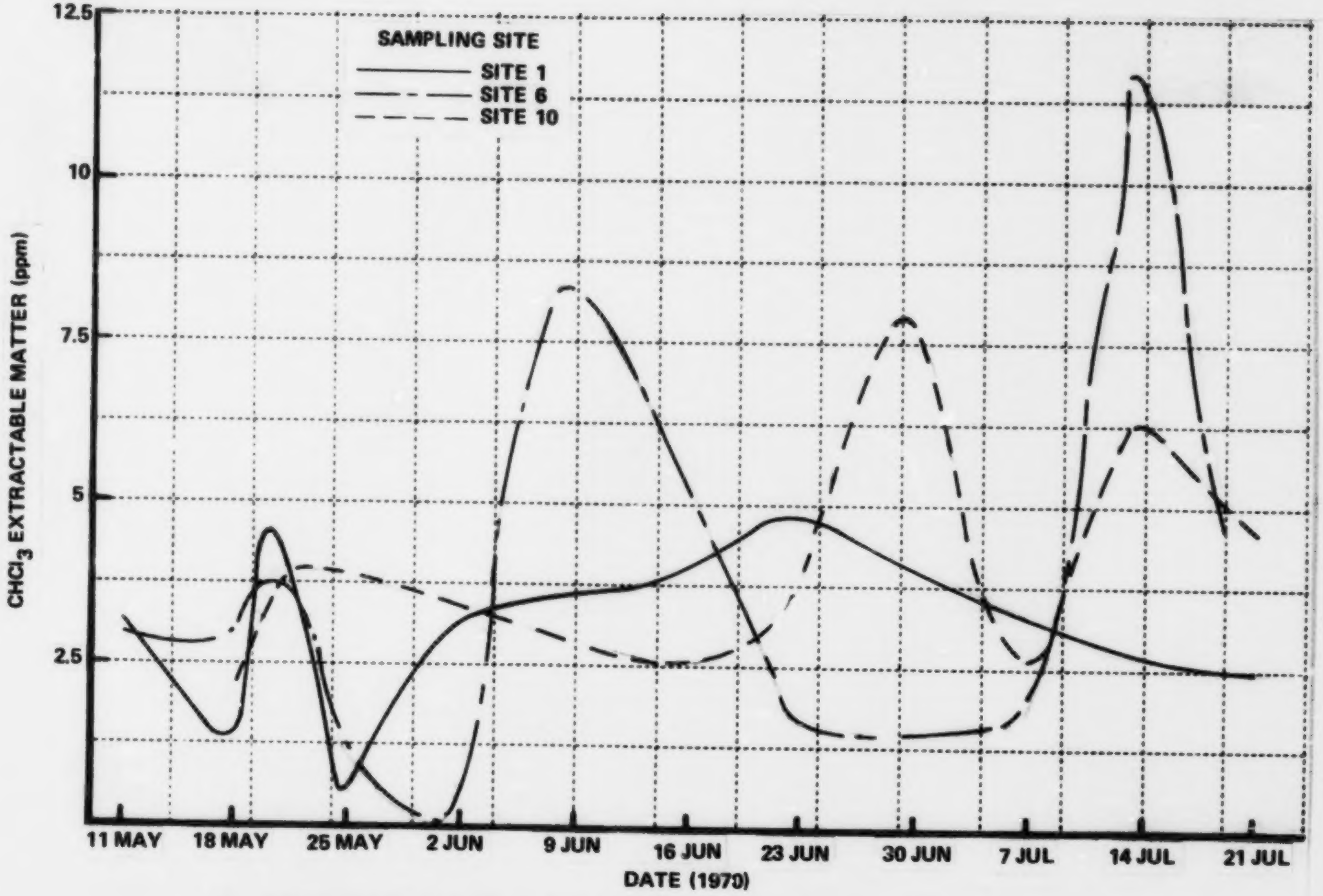

Figure 3 WEEKLY VARIATION IN CHLOROFORM-EXTRACTABLE MATTER FROM SURFACE WATERS OF BUFFALO RIVER

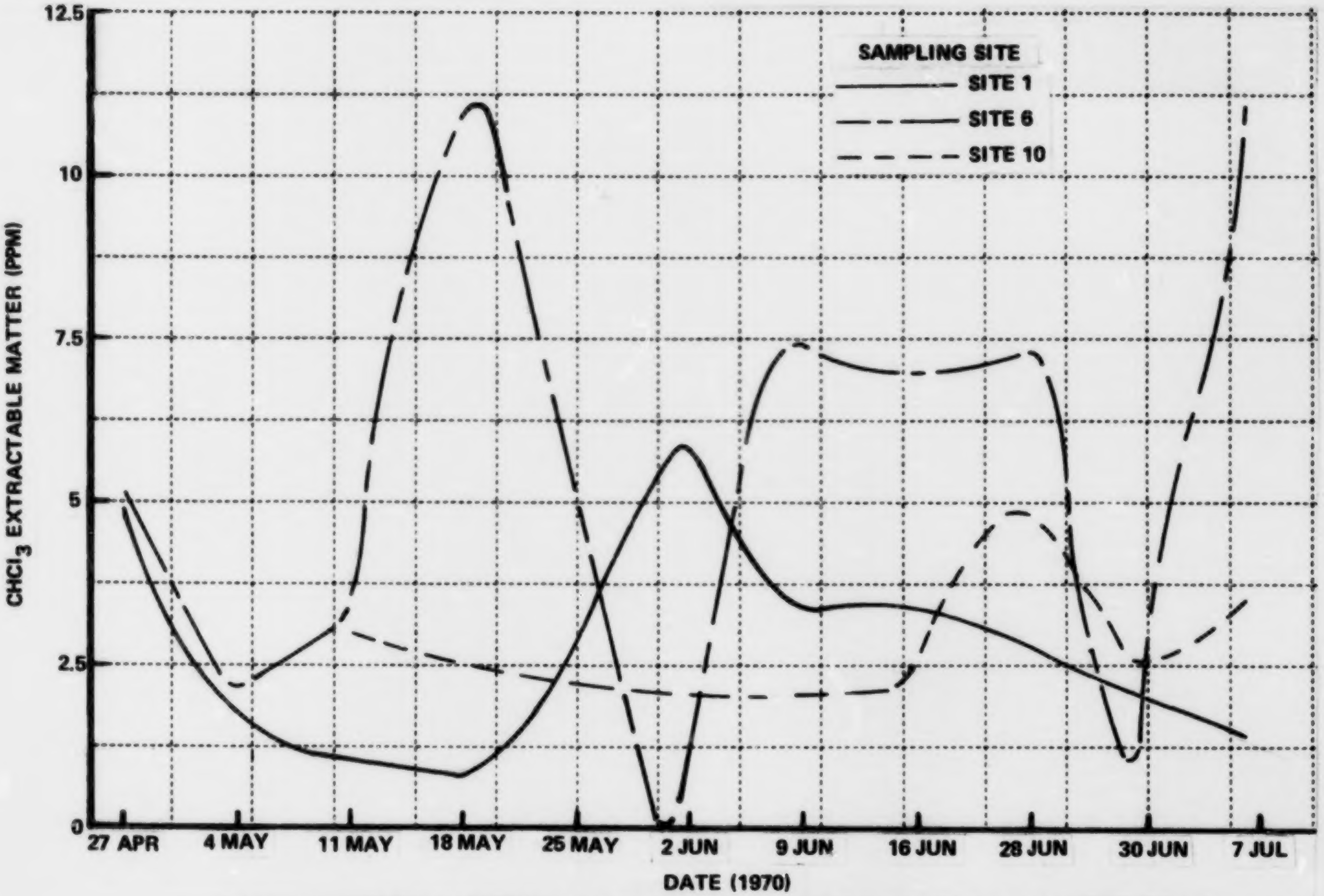

Figure 4 WEEKLY VARIATION IN CHLOROFORM-EXTRACTABLE MATTER FROM BOTTOM WATERS OF BUFFALO RIVER

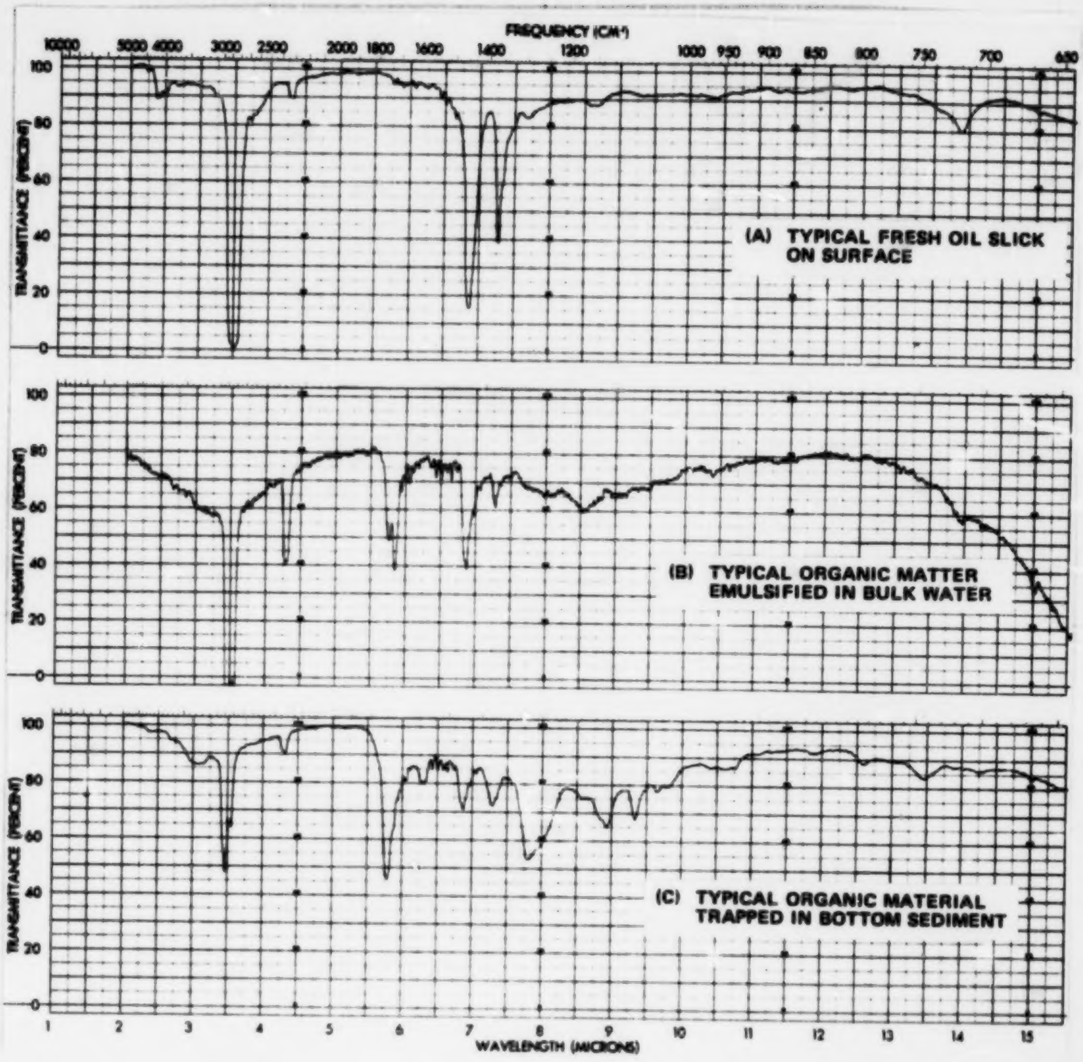

Figure 5 TYPICAL INFRARED "FINGERPRINTS" OF SAMPLES TAKEN FROM BUFFALO RIVER

SAMPLING

This section describes the sampling procedures utilized to determine the oil load in the Buffalo River. The program included the development of new sampling techniques to determine the distribution and quantity of oil on the surface and in the waters immediately below the surface. In the subsections that follow, these sampling methods are described, along with illustrative results of their application.

The 1969 sampling season was devoted almost exclusively to surface sampling. The purpose for the limitation of effort to the immediate river surface and the subsurface waters was to aid in the selection and installation of containment equipment for the river by pointing up the concentration and distribution of oil on the river surface. Several of the surface sampling methods which were developed and used in the river and which are described below proved highly satisfactory.

During the 1970 sampling season, a program of routine weekly sampling of the Buffalo River, both for its surface layers and for the bulk water, was initiated in early spring. Beginning with the week of April 27, 1970, a continuing survey was made to determine the absolute concentrations of pollutants in both the horizontal and vertical planes of the river, and their variability in time. Twelve sampling sites, as indicated earlier in Figure 2, were designated on the basis of their separation from one another, their location with respect to adjacent shoreline industry, and their physical characteristics. These sites did allow adequate characterization of the pollution profile of the Buffalo River as will be described in a subsequent section.

Most samples were taken mid-stream regularly at seven sites and alternately at the remaining five locations. The great number of samples obtained at varying depths at the twelve sites provided a great deal more data than could be easily digested and understood. For this reason, much of the data has been compiled in "Single-Date Summary Charts" in a later section of this report. The remainder are available separately from this Laboratory upon request from the interested reader.

During the 1970 sampling season, as soon as sufficient background data were obtained on the relationships between the pollutant concentrations at the various sites, certain of the sampling sites were given less attention during the routine sampling schedule. In addition, definite limitations on sampling frequency were imposed by the time required to analyze the samples completely. Water was most often taken at the surface, at the three meter depth, and at the bottom. Sampling included use of Kemmerer bottle and a screen as described in the following sections. In addition to the routine collections at the wide distribution of sampling sites, additional work was done to determine the relevance of the depth dimension in measurements of the water-borne pollutants in the Buffalo River. The vertical profile of such waterborne pollutants was investigated in detail at a few sites.

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Throughout the sampling program, major attention was given to documentation of the ability of the various field sampling techniques to retrieve quantitative amounts of oils, water and sediments under various conditions which are expected in all industrial watercourses. Many of the methods for such sampling, field-proven during the program on the Buffalo River, had in addition been calibrated in small pans and in a large, indoor pool. The pool was assembled and used as an oil spill simulation facility during other phases of the overall program. During our field sampling effort, altogether we considered nine sampling techniques, three of which were CAL-developed, one of which had been adapted from a Navy technique, one of which had been adapted from a technique developed by the Scripps Institution of Oceanography, and the others which would fall in the category of "standard water sampling methods."

During the field investigation, a large variety of oils were encountered, and the oils that were encountered were found to be in various conditions as well: they occurred in different film thicknesses, in different states of oxidation and weathering, and with different loadings of debris. Since, in this field program, the number of combinations of variables that were encountered is excessive (since several levels of each variable were found), it is required in future studies to apply some such technique as "random balance experiments" to scan the total problem and enable the selection of those factors which do have major significance on the recovery ratios of the various methods.

Of the numerous oil and water sampling techniques which are presently available for evaluation or actual field use, the nine techniques that were of greatest interest to our particular program (and that covered a wide range of possible sampling conditions) were the following: (1) the prism-dip method; (2) the surface-active hoop technique; (3) the screen-dip technique; (4) the funnel-dip technique; (5) the rotating skimmer technique; (6) the *in situ* freezing technique; (7) the use of a Kemmerer bottle; (8) simple bag sampling; and (9) use of an Ekman dredge. These nine techniques are listed in Table 3, along with major advantages and disadvantages noted during the field use of each technique. The following paragraphs describe the techniques and discuss their applications.

STANDARD METHODS

Bulk water samples were taken throughout the program at points along the River, as indicated in Figure 2. These samples were collected at a range of depths by the use of a Kemmerer bottle having a 1200 ml volume. Sediment samples for oil analysis were gathered with a six-inch Ekman dredge, at the same times and at the same sites as most of the water samples. In addition, bag sampling was carried out by the simple expedient of opening a flattened clean calibrated plastic bag beneath the surface of the water at about a 1 cm depth and allowing it to fill spontaneously. The bag sampling method was also used most often in the course of sampling the outfalls of the various industries. During

Table 3

COMPARISON OF SAMPLING TECHNIQUES USED

SAMPLING METHOD	MOST FREQUENT APPLICATION	ADVANTAGES NOTED	DISADVANTAGES NOTED
PRISM DIP	THIN NATURAL AND POLLUTANT FILMS (0 TO 1 μm); INDUSTRIAL OUTFALLS; SEWER LINES	RAPID; POTENTIALLY CHEAP AND DISPOSABLE; UNIVERSAL; ALLOWED INFRARED IDENTIFICATION OF MATERIALS AS WELL AS QUANTITATIVE AMOUNT FOR THINNEST FILMS	NOT QUANTITATIVE FOR MODERATELY THICK FILMS; ONLY A QUALITATIVE INDICATOR FOR THE CHEMISTRY OF VERY THICK FILMS
SURFACE ACTIVE HOOP	MODERATELY THICK POLLUTANT FILMS (0.1 μm TO 1 cm) ALTHOUGH GOOD FOR THINNER FILMS AS WELL	QUANTITATIVE SAMPLE RECOVERY; BROAD RANGE OF FILM THICKNESSES; REASONABLY LARGE SAMPLE RECOVERY; POSSIBILITY OF GOOD STATISTICS FROM NUMEROUS SAMPLES	DEPLOYMENT IN HIGH WINDS OR HIGH CURRENT DIFFICULT
SCREEN DIP	SURFACE WATERS, "CLEAN" OR OIL-COATED	LARGE SAMPLE RECOVERY; SIMPLE APPLICATION	LABORIOUS TO USE; EASILY FOULED BY WEATHERED OIL AND DEBRIS
FUNNEL DIP	MODERATELY THICK POLLUTANT FILMS (0.1 μm TO 1 cm) BUT SELDOM USED IN FIELD BECAUSE SAMPLE QUANTITY TOO SMALL	RAPID; IMMEDIATE ESTIMATE OF FILM THICKNESS	NOT APPLICABLE TO EMULSIFIED OIL OR DEBRIS-LADEN OIL; VERY LITTLE SAMPLE RECOVERED FOR ANALYSIS; RANGE OF FUNNEL SIZES REQUIRED FOR BROAD UTILITY
ROTATING SKIMMER	SURFACE WATERS, "CLEAN" OR OIL-COATED	LARGE SAMPLE RECOVERY; AUTOMATIC OPERATION OVER LONG PERIODS OF TIME; POTENTIALLY MOBILE	EASILY FOULED BY DEBRIS AND THICK FILMS; REQUIRES EXTERNAL POWER (BATTERY)
IN SITU FREEZING	THICK POLLUTANT FILMS; "CHOCOLATE MOUSSE"; DEBRIS-LADEN FILMS MANY CENTIMETERS THICK	QUANTITATIVE RECOVERY, EXTREMELY THICK AND DEBRIS-LADEN SAMPLES; EASY FIELD DEPLOYMENT; LARGE SAMPLE RECOVERY	LACK OF AVAILABILITY OF FREEZING CHEMICAL AT SOME FIELD SITES
KEMMERER BOTTLE	SUBSURFACE WATERS AT VARIOUS DEPTHS	EASY, ROUTINE DEPLOYMENT	SUBJECT TO ERRATIC OPENING AND DISCHARGE OF SAMPLE AT TIMES
BAG SAMPLES	IMMEDIATE SUBSURFACE WATERS (1-cm DEPTH) AND INDUSTRIAL OUTFALLS	SIMPLE, ROUTINE DEPLOYMENT; BAGS STORE FLAT WHEN EMPTY AND ARE LIGHTWEIGHT	LIMITED TO OUTFALLS OR SURFACE WATERS; OCCASIONAL PROBLEMS WITH LEAKS
EKMAN DREDGE	BOTTOM SEDIMENTS	ROUTINE, RELIABLE METHOD; ADEQUATE SAMPLE SIZE	SUBJECT TO ERRATIC OPENING AND DISCHARGE OF CONTENTS AT TIMES

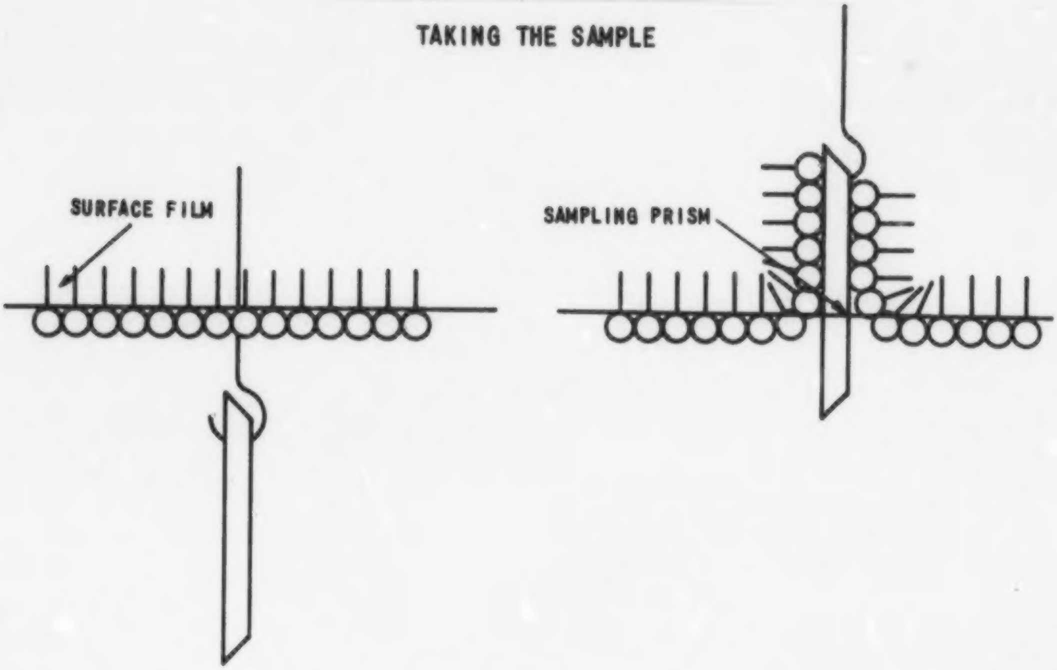
outfall sampling, the sample bag was generally passed from left to right through the outfall stream at a point of its free-fall to obtain a well-mixed representative cross sectional sample. Since these three methods are considered standard water sampling techniques, no further description is warranted in this report.

THE PRISM DIP TECHNIQUE

The dipping of simple prisms, that is, objects about the size and shape of a glass microscope slide, through the contaminated water surface in the river itself, or of an industrial outfall, was the technique of the greatest utilitarian value to this program. The technique itself takes advantage of the availability of a simple analytical method called "internal reflection spectroscopy." The use of the method has permitted rapid acquisition of surface film samples in the Buffalo River and in the Buffalo sewer system, and, more recently, has been extrapolated to the acquisition of natural surface film samples in recreational lakes, unpolluted watercourses, and in the ocean. Figure 6 illustrates the simple method for collecting samples with the prism dip method. The technique is useful both for the measurement of pollutant film thickness and for identification of the pollutants themselves by their infrared "fingerprints." In practice, the internal reflection prisms or plates are simply dipped slowly in and out of the water surface once and are then analyzed in an infrared spectrometer, either immediately in the field or later in the laboratory. The prism dip method transfers the oil layer without significant thickness modifications, no matter how thin the initial layer, to the internal reflection prisms.

When the prisms are analyzed by the internal reflection spectroscopic method, the strongest and most diagnostic infrared absorption band for hydrocarbons occurs in the frequency range from 2950 to 2850 cm^{-1}. The strength of this diagnostic absorption band increases with increasing oil thickness. Using an application of monomolecular layer technology, this increase in infrared absorption with increase in actual film thickness has been calibrated by producing films with thicknesses increasing in increments of approximately 50 Å. An example of the quantification of thickness measurements made with the prism dip technique is presented in an appendix to this report. A calibration chart for film thicknesses ranging from zero up to 1/10 micron is given. Reference to the plot of such calibration data allows an immediate and direct estimate of the thickness actually found at various field sites. For example, in the infrared spectrum of a sample dipped in and out of the Buffalo River which showed a transmittance in the hydrocarbon band of 50% of the incident radiant energy, the calibration chart revealed the film thickness to be approximately 250Å thick when back-referenced to the conditions of the calibration standard. This useful correlation breaks down as the film thickness exceeds 1/10 micron since present prism materials have limited depths of penetration. However, we have experimented with the newer internal reflection prism materials which have a greater depth of penetration and the prognosis for extending the method to

TAKING THE SAMPLE


SURFACE FILM
SAMPLING PRISM

ANALYSIS BY INTERNAL REFLECTION

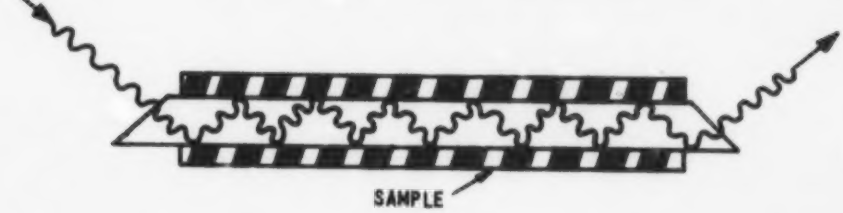


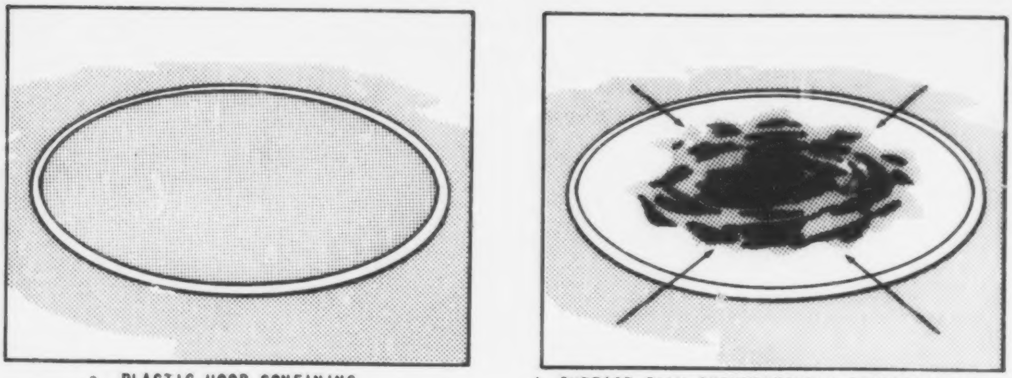
Figure 6 SCHEMATIC OF SURFACE FILM RECOVERY AND ANALYSIS BY INTERNAL REFLECTION METHOD

substantially thicker films is good. On the other hand, the range of film thickness from about 0 to 1/10 micron is the most frequently encountered film thickness in the field and it is this thickness which goes undetected by all other known methods for field detection and field sampling. In fact, during the 1969 and 1970 sampling seasons on the Buffalo River, a film thickness of about 1/10 micron represented the average oil thickness occurring at mid-stream. As enforcement and correction efforts proceed, this thickness will diminish. Thus, samples retrieved by the prism dip technique in the field are expected to continue to be the most useful for estimating pollutant film presence and thickness as well as determining its chemical composition.

THE SURFACE-ACTIVE HOOP TECHNIQUE

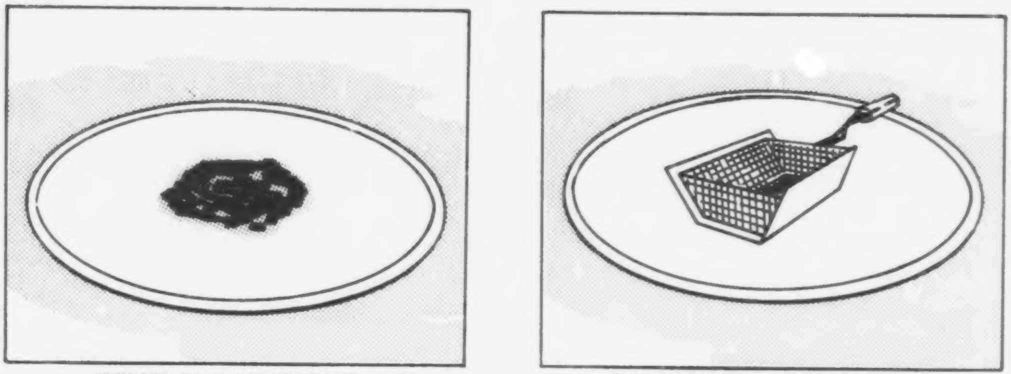
A CAL-developed and field-proved sampling method that has nearly universal utility for the collection of surface oils and other pollutant films is illustrated in Figure 7. This hoop sampling method confines, concentrates and quantitatively recovers surface oil films. In this method, a plastic hoop whose inside surface has been pre-wiped with a surface-active agent is deployed onto the water surface to be sampled. The surface-active agent spreads immediately from the inner surface of the hoop, thereby compressing the resident surface film of oil into a very small thickened area. Filter paper is then used to blot the concentrated film from the surface. By preweighing the filter paper, the sample it recovered (per unit area) can be directly estimated simply by reweighing the filter papers after drying. The amount of surface-active agent involved is so small that its weight is undetectable. Through the use of this method, the equilibrium oil thickness of the Buffalo River during the summer of 1969, for example, was determined to be sufficient to account for only between 100 and 150 gallons of weathered oil. This method has a deficiency in that very light oils, such as No. 2 Fuel Oil (in particular those freshly spilled) are not quantitatively collected because large portions of the sample can evaporate along with evaporation of the water during drying. However, if immediate sample extraction in organic solvent is substituted for drying, this objection is overcome.

Figure 8 shows typical infrared spectra of river surface samples collected before and after oil displacement by the surface-active agent used to wipe the inner periphery of the sampling hoop. This figure shows very clearly that the surface of the water is completely "scrubbed" of oily pollutants by the surface-active material and leaves the water surface essentially clean in a region where an obvious oily pollutant, even a grossly thick slick, had existed. Figure 9 is a collection of illustrations of the filter paper samples (with the compressed oil masses resembling ink blots) which are retrieved by this method from various locations in an industrial waterway. We have noted that the nature of the pollutant film varies strikingly in quantity and in chemical makeup, and that certain repetitive patterns of the compressed masses which are transferred to the filter paper are noted. For example, in Figure 9,



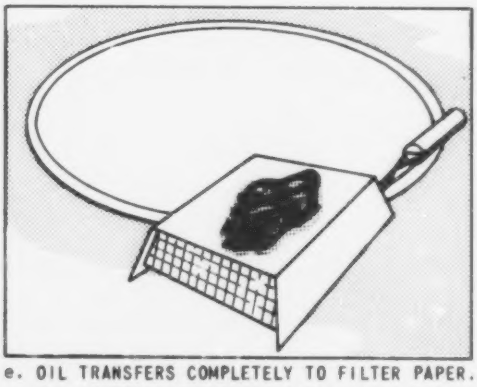
a. PLASTIC HOOP CONFINING KNOWN AREA OF SURFACE FILM

b. SURFACE FILM SPONTANEOUSLY COMPRESSED BY SURFACE-ACTIVE AGENT SPREADING FROM INNER PERIPHERY OF HOOP



c. SURFACE FILM CONCENTRATED INTO THICK POOL AT HOOP CENTER

d. FILTER PAPER ON SPECIAL FRAME IS TOUCHED TO OIL PATCH



e. OIL TRANSFERS COMPLETELY TO FILTER PAPER. AND IS READY FOR QUANTITATIVE ANALYSIS

Figure 7 TECHNIQUE FOR OIL FILM CONFINEMENT, CONCENTRATION AND QUANTITATIVE RECOVERY

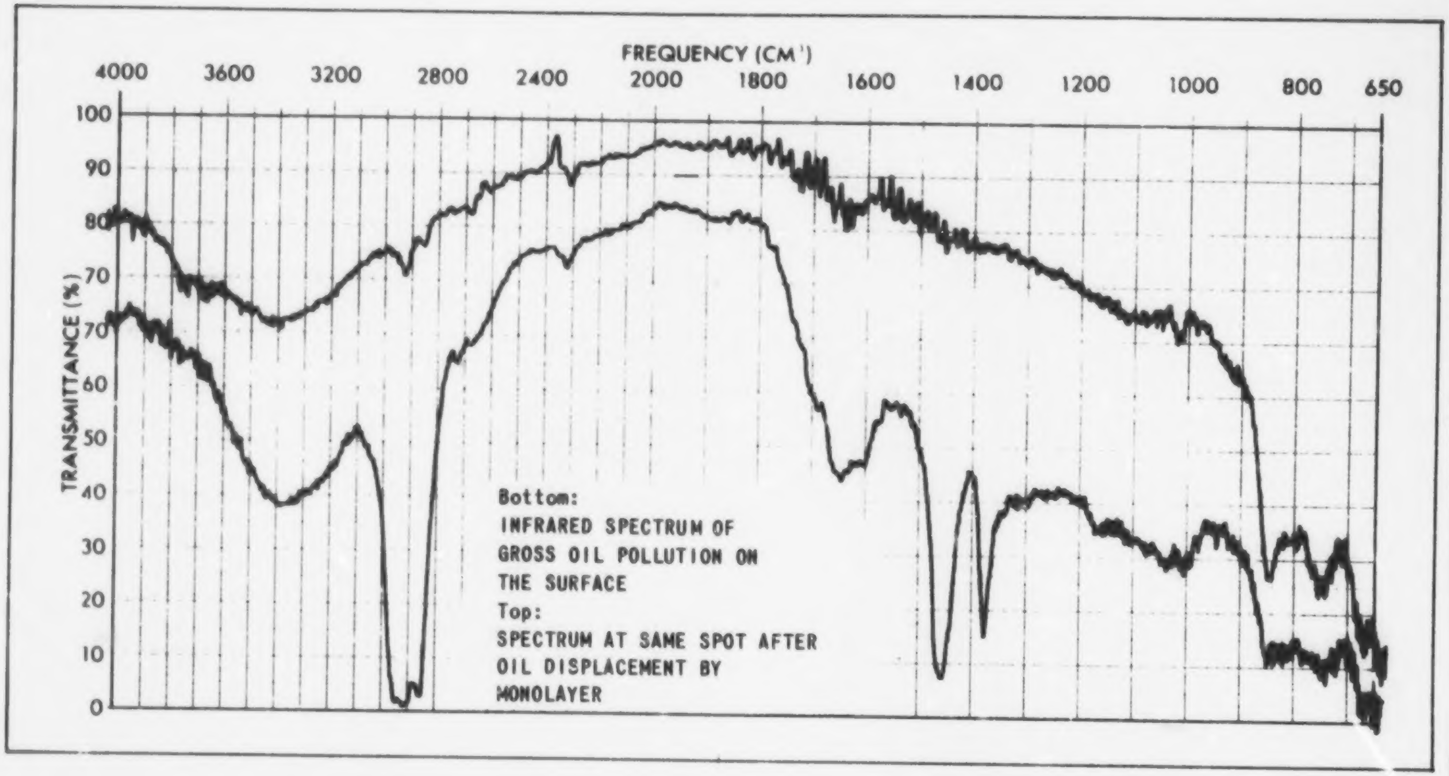
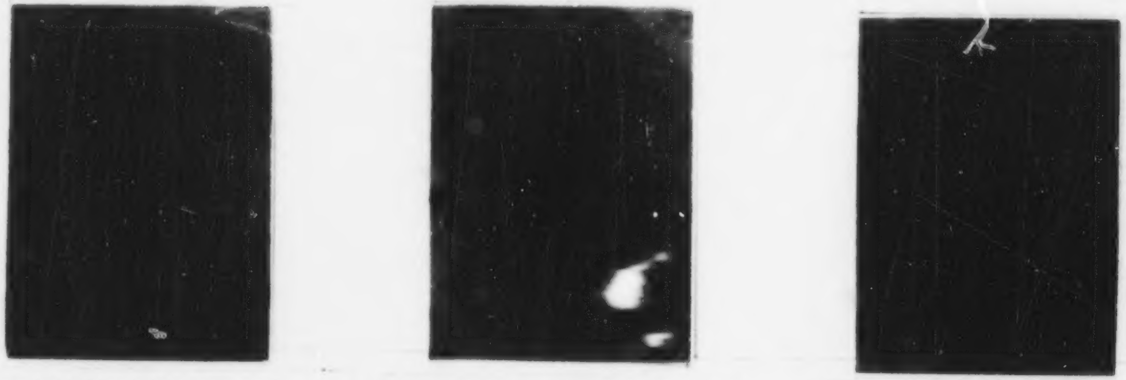


Figure 8 INFRARED SPECTRUM OF RIVER SURFACE BEFORE AND AFTER OIL DISPLACEMENT BY SURFACE-ACTIVE AGENT

NATURAL TRAP AT SOUTH PARK BRIDGE (~2.2 GRAMS)

MID-STREAM AT SOUTH PARK BRIDGE (~0.4 GRAM)

MID-STREAM NEAR NATIONAL ANILINE PLANT (< 0.1 GRAM)



MID-STREAM NEAR MOBIL OIL PLANT (~0.1 GRAM)

MID-STREAM AT MICHIGAN AVENUE LIFT BRIDGE (~0.2 GRAM)

IN CURRENT FROM AIR BARRIER (< 0.1 GRAM)

Figure 9 NEAR-QUANTITATIVE OIL SAMPLES FROM CONFINED AREAS OF THE BUFFALO RIVER (RETRIEVED WITH AID OF SURFACTANT-WIPED PLASTIC HOOPS)

a freshly spilled oil such as that illustrated in the upper left-hand corner labeled "Natural Trap at the South Park Bridge" gives a very black and diffusing "ink spot," whereas an oil slick that is very highly weathered, and indeed almost cross-linked, gives a wrinkled and thin, almost "crumpled plastic" pattern as illustrated in the bottom center photograph labeled "Midstream at the Michigan Bridge."

For further analysis, the retrieved oil films, after being weighed, are simply extracted from the filter paper by a solvent, typically chloroform. The samples shown in Figure 9 have been analyzed in this manner and are discussed in the ANALYSIS section. Figure 10 is a collection of infrared spectra of typical surface pollutants as quantitatively sampled by this hoop method. This figure illustrates the general utility of the technique for different types of oils and different situations. It is equally able to concentrate and collect fresh oil and weathered oil, and even weathered oil containing large amounts of extraneous matter and debris.

THE SCREEN SAMPLING METHOD

While the hoop method is very surface-specific, leading to the recovery of all materials at the air-water interface or floating upon it, we were also very much interested in the concentration of oily pollutants that might be present in the immediate subsurface water layer. In particular, in order to be successful in removing the obvious pollutant films from a large region during oil skimming or displacement by any other mechanism, it is necessary to assure that oils in the immediate subsurface waters are not available to rapidly repollute the region simply by spontaneously collecting at the cleaned interface. To evaluate the extent of this problem in the Buffalo River and also to evaluate the subsurface sampling method itself, we selected a screen sampling technique introduced by a group at the Naval Research Laboratory some years ago. Figure 11 shows one simple screen device which embodies this concept and which is typical of the type used on the Buffalo River for the 1969 and 1970 sampling efforts.

To collect samples, this screen is simply touched to the water surface, lifted, and tilted so that the captured water (which has been estimated to represent only the top 0.04 cm of the surface water) is allowed to drain to one corner, where it runs off into sample collection bottles. Typical collections at a relatively clean location (Michigan Avenue Bridge in the Buffalo River) showed water with a total oil and fat content of about 18 milligrams per liter, while the content from subsurface water at depths of from 7 to 21 feet (collected using a standard Kemmerer bottle) averaged only about 4 milligrams per liter of the same organic pollutants. At a relatively polluted location (beneath the South Park Bridge in the Buffalo River), the screen-collected sample at the surface showed the remarkably high oily pollutant content of some 86 milligrams per liter while the sample at the 2 m depth, taken with the Kemmerer bottle, showed only 7 milligrams per liter and a similar sample taken at a 7 m depth showed only 2 milligrams per liter.

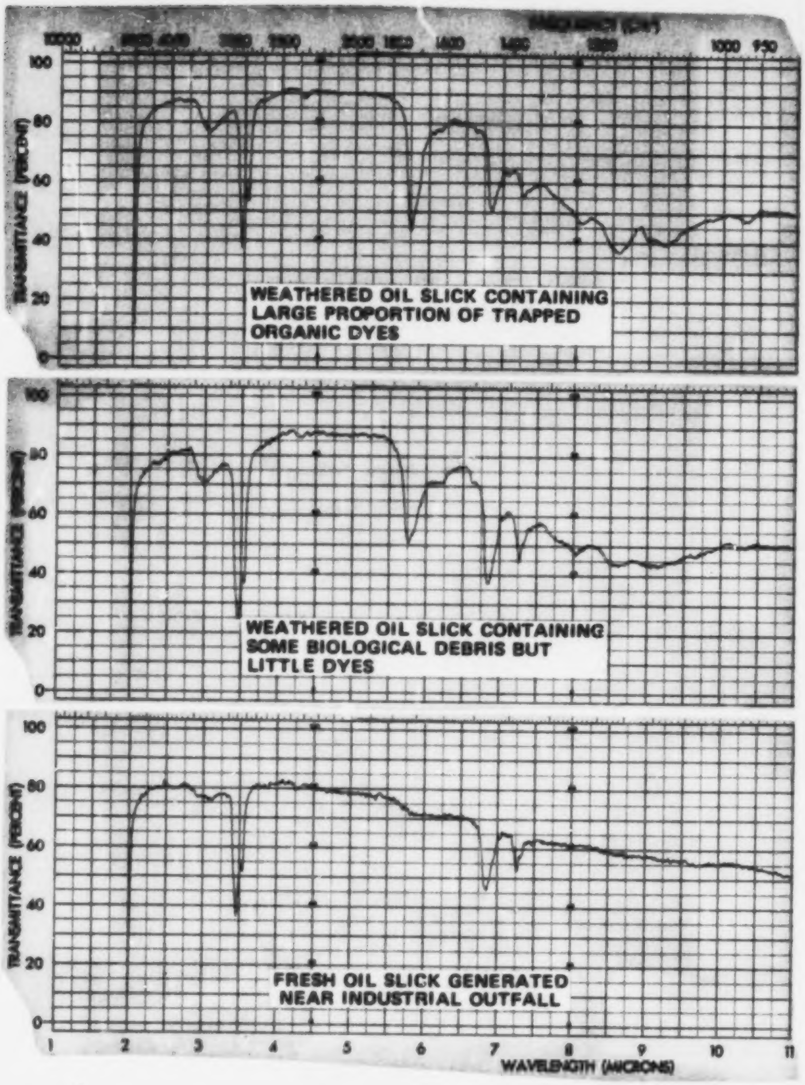


Figure 10 INFRARED SPECTRA OF SURFACE POLLUTANTS QUANTITATIVELY SAMPLED BY THE "HOOP" METHOD, ILLUSTRATING GENERAL UTILITY OF THE TECHNIQUE BOTH FOR FRESH OIL AND FOR WEATHERED OIL CONTAINING EXTRANEOUS ORGANIC MATTER AND DEBRIS

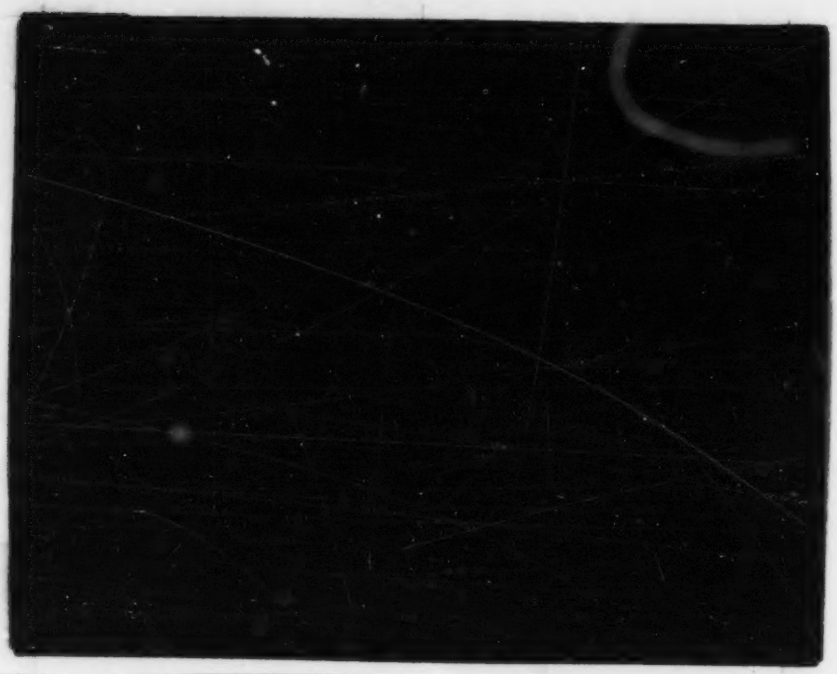


Figure 11 SAMPLING SCREEN USED TO COLLECT SURFACE POLLUTANTS

Results of this nature demonstrate that at least one industrial waterway, and by extrapolation all industrial waterways, support considerably larger surface burdens of oily wastes than is apparent from the films thinly spread over the water surface, and which are usually so thin as to show interference colors. However, the screen method of sample recovery is laborious and time-consuming. Similarly useful subsurface samples can be obtained semi-automatically with the aid of a small rotating drum unit developed first at the Scripps Oceanographic Institute. This rotating skimmer technique is described in a following subsection.

It is pertinent at this point to intercompare the methods already discussed. Table 4, for example, presents a comparison of the oil amounts recovered by the screen method and by the hoop methods when applied simultaneously at the same sites in the Buffalo River on a given day. By comparison of the vertical columns in Table 4, it can be seen that there is very little correlation between the screen-collected samples and the hoop-collected samples. This dramatizes the fact that the two techniques actually collect different qualitative types of material. The screen, in particular, collects subsurface water; the hoop collects "above-surface" oil films. It is only in that special case, illustrated by the first row in Table 4, when fresh slicks of light oils are present that the screen method simultaneously collects both the surface oils and the subsurface water, and a reasonably high proportion of oil in the collected sample is measurable. In the other instances, the subsurface water can show very little indication of chloroform-extractable matter (oils and fats), even in the presence of a very noxious and thick oil slick, because the oil slick is weathered, oxidized and cross-linked to itself and to debris also present in the slick. The comments column in Table 4 indicates the nature of the surface slick present at each of the sites during this simultaneous sampling by the two techniques.

Table 4

COMPARISON OF OIL RECOVERED BY THE "SCREEN" AND "HOOP" METHODS FROM THE SAME SITES IN THE BUFFALO RIVER ON THE SAME DAY

SAMPLING SITE NO. (REFER TO FIGURE 2)	CHLOROFORM - EXTRACTABLE MATTER IN SAMPLE RECOVERED		COMMENTS
	BY "SCREEN"	BY "HOOP"	
1	$\sim$3 PPM IN SURFACE WATER	$\sim$ 0.02 g/m^2 SURFACE FILM	FRESH SLICK OF LIGHT OILS READILY RECOVERED ON SCREEN ALONG WITH SURFACE WATER; OILS FLOWED TO "RE-HEAL" SURFACE AFTER EACH SCREEN DIP
5	$<$1 PPM	$\sim$ 0.03 g/m^2	THICK, WEATHERED OIL SLICK AT THIS SITE IMMEDIATELY COATED SCREEN ON FIRST DIP, AND DID NOT TRANSFER WITH WATER; WEATHERED OIL DOES NOT READILY FLOW TO RE-COVER SPOT WHERE SCREEN REMOVED ORIGINAL LAYER
6	$<$ 1 PPM	$\sim$ 0.02 g/m^2	WEATHERED, CROSS-LINKED POLLUTANT SLICK AT THIS SITE
9	$\sim$ 1 PPM	BETWEEN 0.01 AND 0.02 g/m^2	THINNER, BUT STILL WEATHERED OIL SLICK AT THIS SITE

Table 5, on the other hand, provides a comparison of the quantities of chloroform-extractable matter in samples of the Buffalo River surface water collected simultaneously by the screen method and the more traditional "bag" method. The "bag" method is similar to that which might be called a "jar" method or a "can" method, or just a "grab sample" method, in which a container is opened immediately subsurface to the interface and the water allowed to run in. In the "bag" technique, the collected sample is not as surface-specific as is desired. Comparison of the second and third columns in Table 5 shows very clearly that in each and every instance, the screen dip sample had approximately twice the concentration of chloroform-extractable matter as that in a 1 cm subsurface bag sample. The more detailed the analysis of the oil pollution problem, the more apparent it becomes that natural water bodies are stratified in terms of the location of the highest concentrations of oily pollutants. This stratification begins at the air-water interface where the oil concentration is the highest, and in the immediate subsurface zones certainly not extending many centimeters below it.

Table 5

COMPARISONS OF QUANTITIES OF CHLOROFORM-EXTRACTABLE MATTER IN SAMPLES OF BUFFALO RIVER SURFACE WATER COLLECTED SIMULTANEOUSLY BY THE "SCREEN" AND "BAG" METHODS

SAMPLING SITE NO. (REFER TO FIGURE 2)	DATE (1970)	PPM OF EXTRACTABLE MATTER	
		SCREEN-DIP SAMPLE	1-cm SUBSURFACE BAG SAMPLE
11	8 JUNE	3.8	2.0
1	22 JUNE	4.8	1.1
5	22 JUNE	14.3	7.9
8	22 JUNE	6.1	2.5
1	29 JUNE	4.2	2.6
5	29 JUNE	3.6	3.2
8	29 JUNE	4.0	<1

THE FUNNEL DIP TECHNIQUE

The inverted funnel method, illustrated in a sequence of photographs in Figure 12, is a very simple and rapid oil collection and thickness measuring scheme which was found useful in a preliminary test series at CAL, but was not found very useful in field work. We describe the technique briefly here for the sake of completeness.

The sampling funnel is generally cleaned in a hot soap solution, and after a quick towel drying of its outside surface, is slowly dipped (large end first) into the water. Any surface oil present is driven toward the center of the funnel and as the funnel is continually lowered, the oil collects in the stem. When the stem end of the funnel is sealed by finger pressure, the oil column will remain in the stem end after the funnel is lifted out, even though in most instances it has been noted that the bulk of the liquid in the wide end of the funnel is immediately lost. The length of the column of oil can then

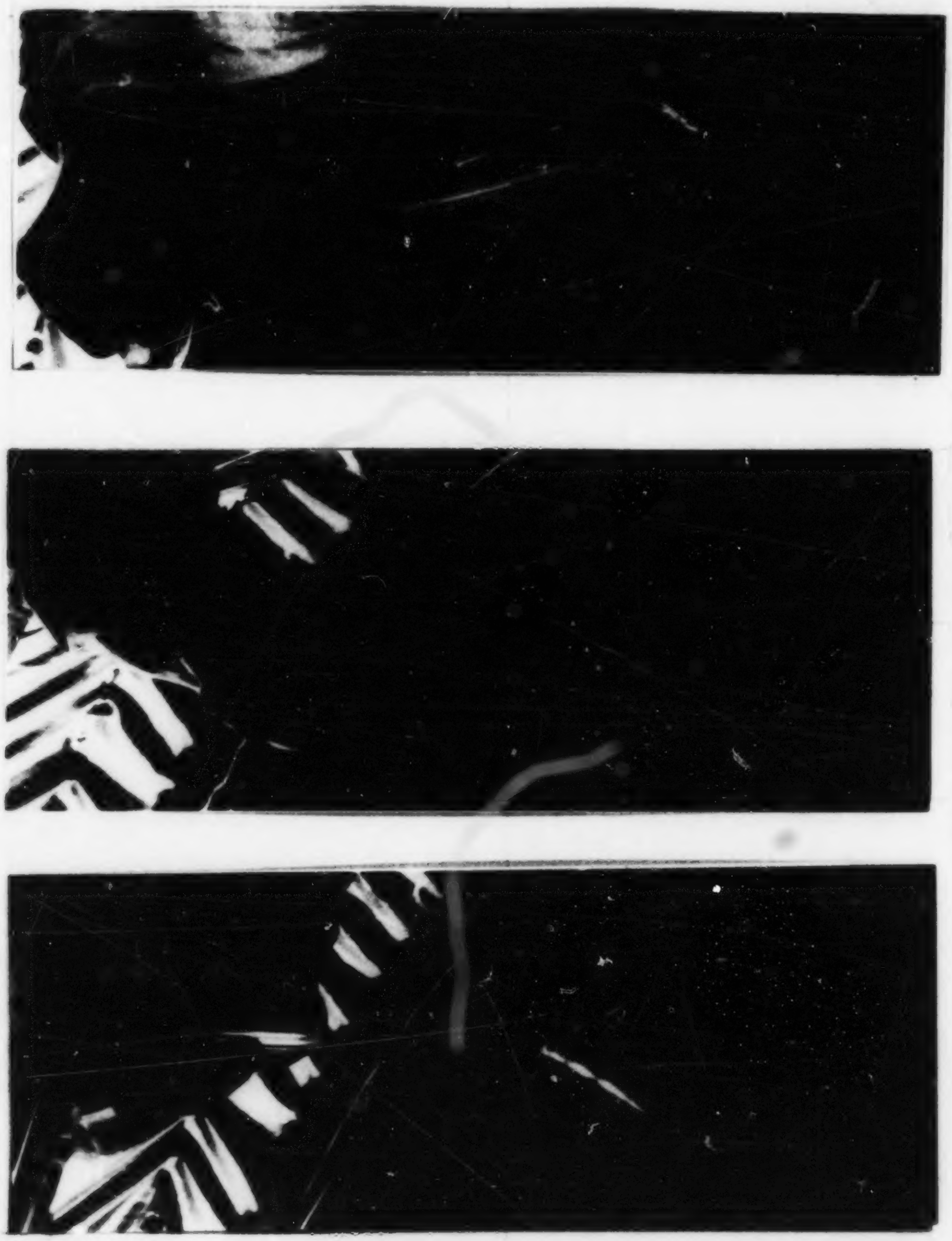


Figure 12 FUNNEL DIP TECHNIQUE

be measured with a rule or directly in the pre-calibrated stem. The length of the oil column multiplied by the ratio of the stem area to the funnel area provides a rapid estimate of the actual film thickness present. To cover the thickness range of 0.001 mm to 1 mm with funnels of manageable stem length (under 25 cm) and with the hope of obtaining a measurable column height (say, 1 mm), funnels with area ratios of 1/1,000 and 1/250 can be used. For thinner or thicker films, other funnel geometries can be selected.

This method does not work well for weathered oils, debris-laden films, or emulsified surface layers.

THE ROTATING SKIMMER TECHNIQUE

Evaluation of the various specimen collection techniques also included the construction and testing of a rotating drum skimmer based upon our own simplification of the design originally presented by the Scripps Institution of Oceanography. Figures 13 and 14 show photographs of the sample skimmer in the configuration in which it was used in the Buffalo River. Sample collections are made by a rotating drum whose surface is readily wetted by water, and a wiper blade which is pressed tightly to the surface of the drum to remove both the water and any pollutant film as the drum rotates. The collected sample runs along the wiper blade into three plastic hoses and three separate collecting bags. Both the cylinder and the wiper are relatively easy to clean when the sampler is used in waters free of weathered oils. The skimmer is battery-powered.

During field operation, the skimmer was either mounted along shore in a stationary position or pushed ahead from a small boat at a low speed. The skimmed surface water sample was estimated to represent only the uppermost fraction of an inch of the water, as in the case of the screen sampling method. As an alternative to the three separate collecting bags, a large polyethylene bottle was used at slightly less than atmospheric pressure to collect the sample. Since there was no pump in the liquid line and since the plastic was readily replaced, the system was expected to be relatively easy to clean between operations. However, the weathered and debris-laden oil encountered routinely in the Buffalo River completely frustrated the purposes of this device and it was not useful for sample collection to any extent.

In use, the cylinder (15 inches in diameter, 24 inches in length, and operated at 9 rpm) collected thicknesses of oil and water which depended only to a limited extent on the operating characteristics and to a major extent on the quality of the surface film actually present. In the operation of this sampling device in calibration experiments in the laboratory, where fresh oil was used, the pick-up thickness could be calibrated by making standard films of known thickness and measuring the volume collected per unit time and dividing by the total area. In

Figure 13 SAMPLING SKIMMER – FRONT VIEW

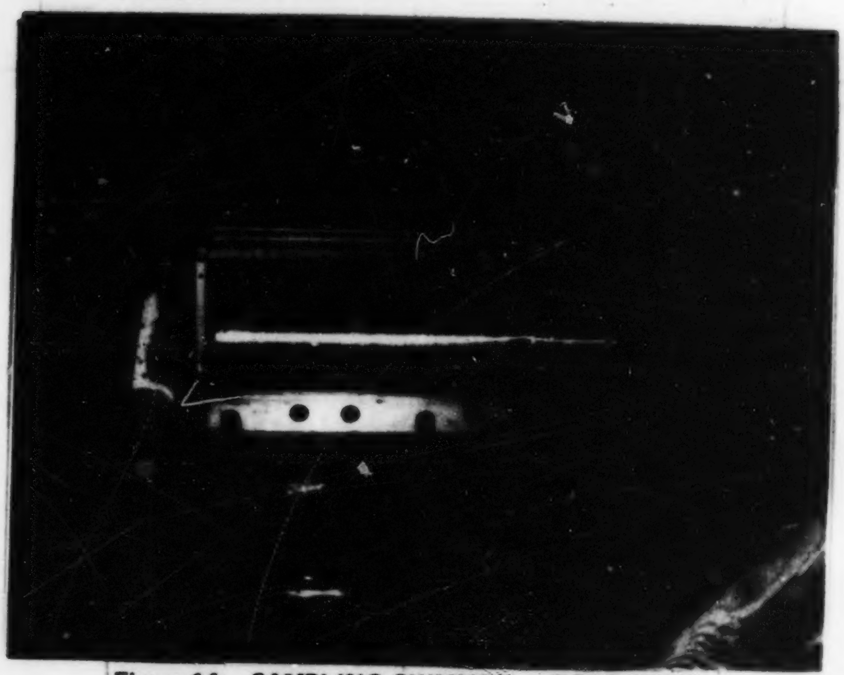


Figure 14 SAMPLING SKIMMER – REAR VIEW

principle, the rotating skimmer surface sampler makes possible rapid collection of large volumes of relatively undisturbed water and surface films from about the upper 100 microns of the water surface. At a reasonable rotation rate, an area of about 1000 square meters can be easily sampled in an hour and this makes the technique more than competitive with the sample screen technique. The method, however, has the same problems encountered with the metal screens in the screen dip technique: easy fouling by debris and greases, along with the usual difficulties of metal devices in water. It does, however, allow a collection of a surface layer with a minimum of vertical mixing.

Figure 15 is a photograph of the rotating skimmer coated with congealed grease from a typical oil slick in the Buffalo River. This illustrates the major failure of this unit as a surface sampler for industrial watercourses. That is, in the presence of weathered oil, the collected oil slick congeals into a very thick mass which will not even fall from a vertical wall. Therefore, sample collection becomes very nonquantitative and clean-up of the devices becomes more time-consuming than worthwhile.

Figure 15 PHOTOGRAPH OF ROTATING SKIMMER COATED WITH CONGEALED GREASE FROM NATURAL OIL SLICK, ILLUSTRATING FAILURE OF UNIT AS SURFACE SAMPLER IN THE PRESENCE OF WEATHERED OIL

On a few occasions, the rotating sample skimmer did allow samples to be sufficiently and rapidly collected from a number of locations in the Buffalo River and these samples were analyzed to estimate the oil to water recovery ratio. In all instances, the oil which was collected congealed into a thick grease, therefore this recovery ratio was not found to be meaningful. It is suggested that follow-on research be undertaken to compare samples collected by the rotating drum method and the screen-dip method so that a decision can be made as to which of the two units should be deployed in an oil spill where the oil is fresh and would respond to pick-up by either of the two methods.

THE *IN SITU* FREEZING TECHNIQUE

It was expected that our efforts in oil sampling would be directed almost completely to developing routine methods to retrieve, for quantitative analysis, pollutant films from near zero thickness to only a few millimeters thick. However, conditions on the Buffalo River necessitated development of techniques for very thick oil film sampling as well. The techniques already described in this section were completely inadequate for thick emulsified and debris-laden layers of oil found in the River at certain natural concentration points or collected along booms. Similarly, these techniques have been known to fail with the oil layers characterized as "chocolate mousse" often encountered in oil spills at sea.

In the Buffalo River, significant quantities of oil were found accumulating in slicks sometimes more than three inches thick along various lengths of the shoreline and at artificial collecting booms. This agglomerated oil and debris posed the difficulty of retrieving representative samples from defined surface areas. At the booms, the sampling was further complicated by the presence of a considerable quantity of oil-soaked debris admixed with the oil and grease.

Figure 16 illustrates simple, inexpensive equipment developed at CAL as a solution to this sampling problem. This equipment has extended our capabilities for quantitative recovery of oil from films a few centimeters thick to films many inches thick and beyond, even though these slicks are very heterogeneous in character and contain debris of large and irregular sizes. Stiff aluminum frames, open at the top and bottom, were fabricated. These forms contain a known slick surface area as they are placed on the polluted water surface. The aluminum form, which we found in normal operation to sink to the full depth allowed by its design, occasionally had to be forced through the debris-loaded grease accumulations. Once the form was in place, the contained oily mass was immediately solidified by pouring liquid nitrogen into the upper opening of the form. Again, as an operational detail, it was learned that simple thermos bottles filled with liquid nitrogen the morning of the sampling day were adequate to handle most sampling needs over an eight-hour period. When the liquid nitrogen was poured from the thermos container into the upper opening of the form, the aluminum frame was such a good thermal conductor that the oily mass was quickly frozen to the form periphery. In most cases, very little water below the pollutant slick was trapped frozen to the solidified oil and debris, apparently because of the high specific heat of the water and low conductivity across the water-oil interface. The frozen samples were simply lifted from the water surface with tongs and placed in storage containers for later weighing and analysis in the laboratory.

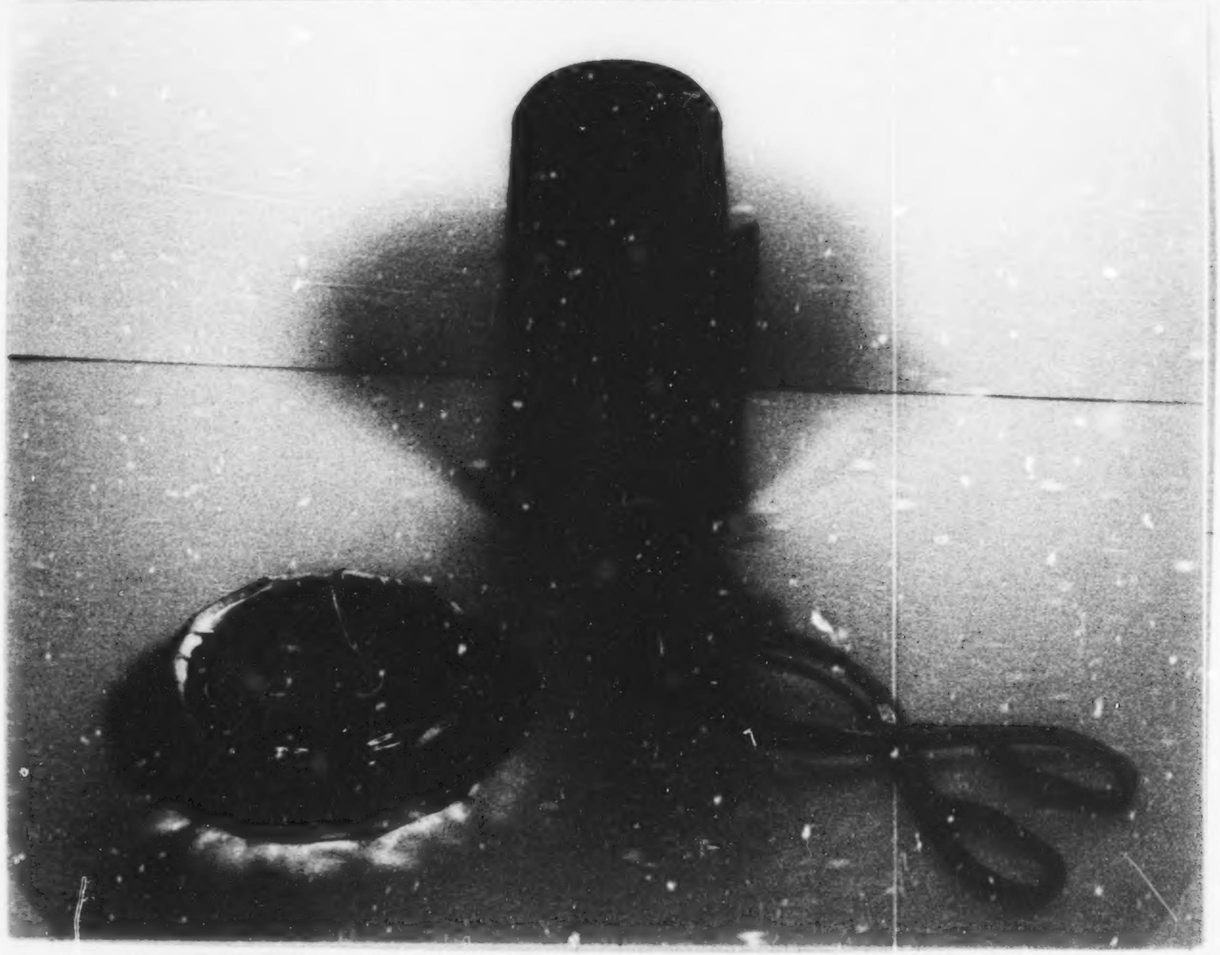


Figure 16 SIMPLE EQUIPMENT FOR QUANTITATIVE RECOVERY OF THICK OIL ACCUMULATIONS

One example of the field use of the method is cited here for illustrative purposes. During November 1969, thick oil slicks regularly accumulated at the collecting booms installed across the upper Buffalo River. Similar thick oil and debris accumulations were noted along the upper River shoreline. Sampling with the equipment illustrated in Figure 16 resulted in an average yield of 2 lb/ft^2 of pollutant slick. The value was later corrected for the approximately 20% water which could be separated from the oily mass, but included the weight of the oil-soaked debris, including leaves, which was collected admixed with the thick grease, oils and, sometimes, even crystallized dyes. The boom at which the sampling occurred spanned a 200 foot wide portion of the Buffalo River, and the contained oil and debris mass extended an average of 6 feet from the boom. This nearly 1200 square feet of trapped pollutants included then, about 2400 lb of oil and floating oil-soaked debris. If the oil is considered to have an average density of about 8/10 that of water, this weight of oil would correspond to about 360 gallons of oil trapped at this boom alone. Other sites with equally thick and extensive accumulations gave evidence that perhaps some 1000 gallons of floating oils, greases, and oil-soaked debris were trapped naturally in the upper Buffalo River, along its shoreline.

Figure 17 shows typical infrared spectra of materials making up these extensive accumulations. Both the oil masses trapped at the manmade barriers and in the pollutant slicks along the undulating shoreline of the Buffalo River showed infrared absorption characteristics typical of oxidized hydrocarbons. In addition, the infrared spectra of the frothy accumulations collected by this *in situ* freezing technique along the shoreline during 1969 and 1970 often showed absorption bands characteristic of the effluents, mainly green and red dyes, from a major chemical plant.

A failure of the *in situ* freezing method is that thin oil films on the order of one millimeter or less do not sufficiently insulate the water substrate from the liquid nitrogen. In these cases, water freezing and extraneous water collection are noted.

SUMMARY

A qualitative comparison of the sampling techniques used is given in Table 3. In this table, each sampling method used is listed along with its most frequent application. Significant advantages and disadvantages which were noted during field use of the methods are also specified. As a result of our development and use of these sampling techniques, it is recommended that further research be considered for an intercomparison of the following methods: (1) the prism-dip technique, (2) the surface-active hoop technique, (3) the funnel dip technique, (4) the screen sampling technique, (5) the rotating skimming technique, and (6) the *in situ* freezing technique. It is recommended that at least four oils be tested with each of the methods; for example, No. 2 Fuel Oil, No. 6 Fuel Oil, Bachaquero Crude Oil, and South Louisiana Crude Oil. Although

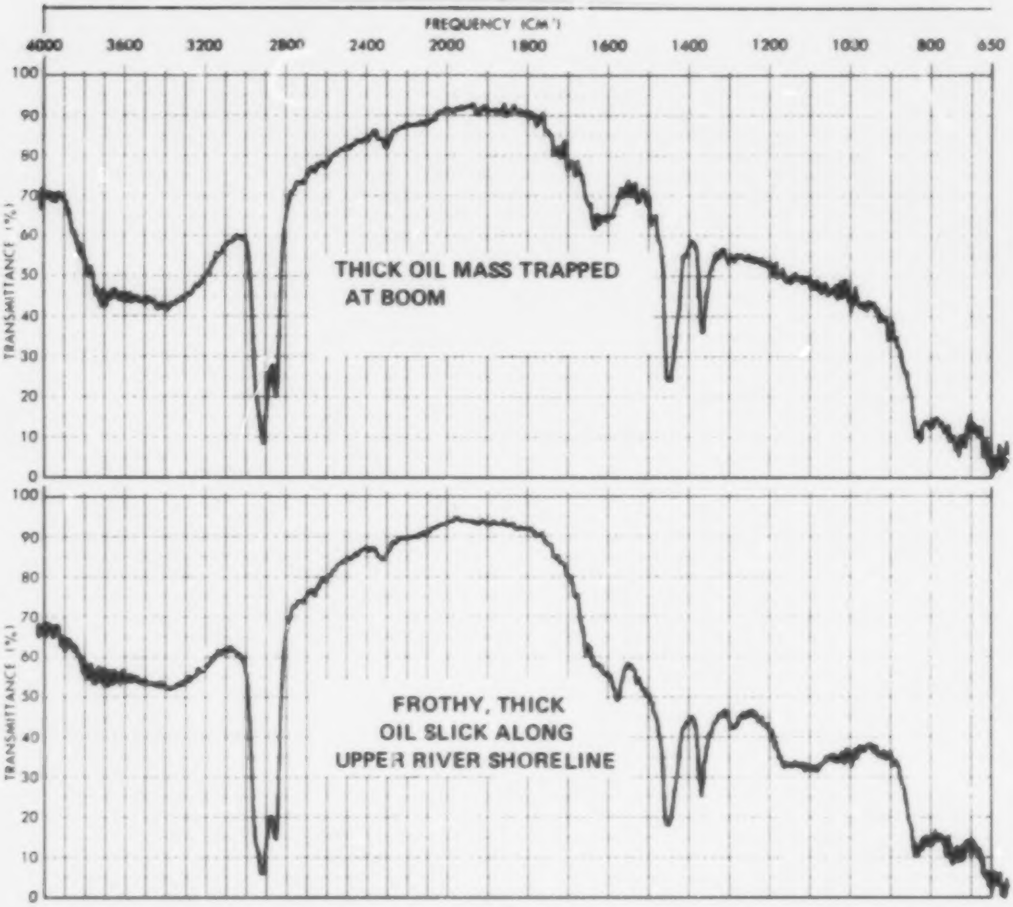


Figure 17 CHARACTERISTIC INFRARED SPECTRA OF OILY POLLUTANT MASSES IN THICKNESSES EXCEEDING 3 INCHES

there will be great difficulty in studying the effects of the many combinations of controllable or input variables on the oil removal or oil collecting potential of the sampling and recovery schemes presented here, it is not necessary to study the entire gamut of combinations. For example, thousands of trials can be eliminated if a "random balance" type experiment is designed to reduce the number of trials required and to find which of the factors (oil type, oil thickness, etc.) might be rapidly eliminated.

ANALYSIS

Samples taken during the 1969 and 1970 sampling programs on the Buffalo River were analyzed for each of the following parameters where appropriate:

1) pH
2) solvent extractable material
3) dissolved solids
4) ultraviolet/visible spectra
5) infrared spectra of residues from the samples themselves and of their solvent extractable material
6) gas chromatograms.

In special instances the following measurements were made:

1) atomic absorption spectra (for trace metals)
2) surface tension (obtained to address questions of potential emulsification).

In addition, dissolved oxygen and temperature were measured in the field during the 1970 sampling program.

Instrumentation used in the conduct of the above chemical characterizations and analyses included (1) a Corning Model 12 pH meter, (2) a Mettler S-5 weighing balance, (3) a Bausch and Lomb Spectronic 600/ Ultraviolet-Visible Spectrophotometer with VOM-5 recorder and a Beckman DK-2 UV/Visible recording spectrophotometer, (4) Perkin-Elmer infrared recording spectrophotometers, Models No. 21, 457, and 700 in both the normal transmission and internal reflectance modes, (5) a Hewlett-Packard Model 5750 gas chromatograph and a Perkin-Elmer Model 881 gas chromatograph, (6) a Perkin-Elmer Model 303 atomic absorption spectrophotometer, (7) a Cenco tensiometer and Rame-Hart contact angle goniometer, and (8) a Model 51 Yellow Springs Instruments dissolved oxygen and temperature probe.

The majority of the samples which were included in the analysis program would fall into one of the five following categories: (1) bulk water samples, (2) surface film samples recovered with use of the sampling hoop, (3) industrial outfalls, (4) bottom sediments, and (5) shoreline deposits.

SELECTION AND DEVELOPMENT OF A STANDARD METHOD FOR ANALYSIS OF SAMPLES FROM AN INDUSTRIAL WATERCOURSE

Early in this program, a standard ASTM method based upon hexane extraction of industrial waste waters, followed by column adsorption techniques, had been considered to be the most likely to succeed on the

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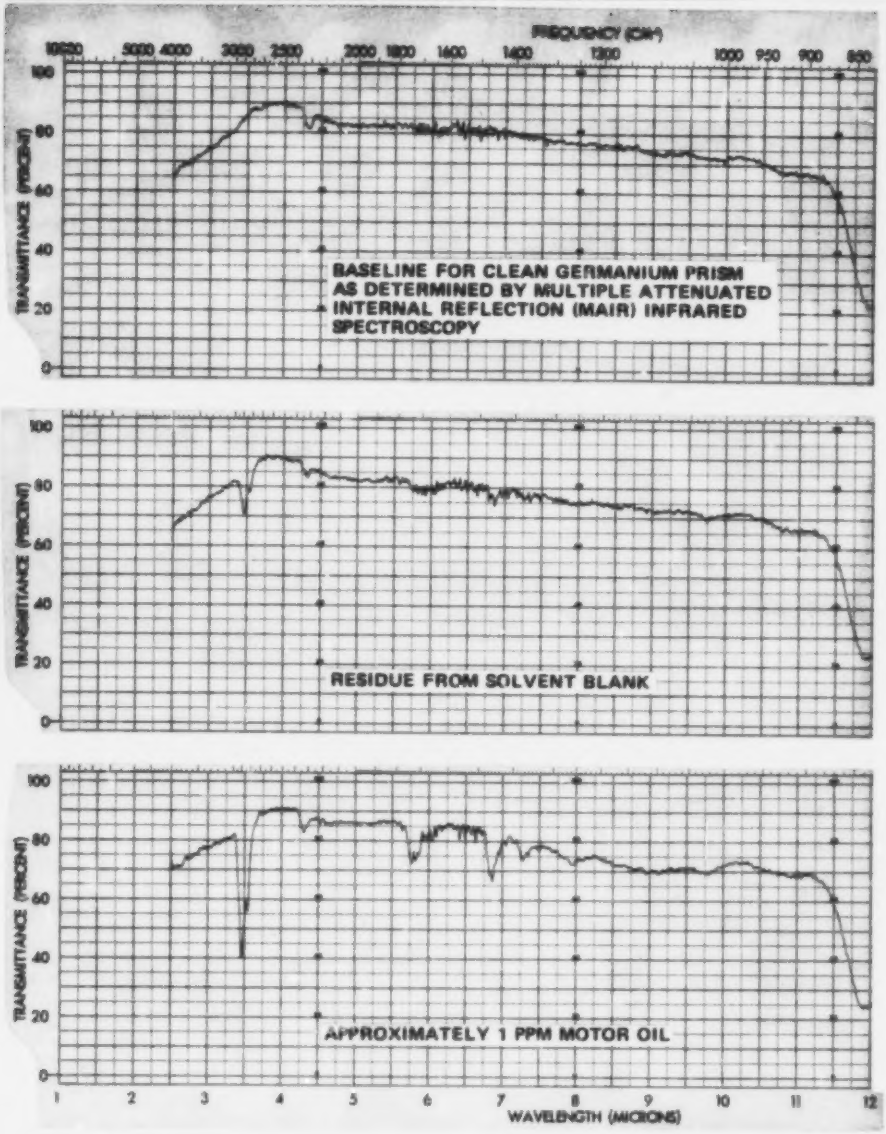
basis of experience related to us informally by other groups. As the program proceeded during late 1968 and early 1969, evidence accumulated from other phases of the program which indicated that many of the major oily pollutants known to be present were either not detected or not differentiated by this standard method. Problems that were found included insolubility of some of the components in hexane and also inadequacy of material separation by column filtration. Therefore, a major early task in the analytical program was the development of a reliable combined chemical-instrumental method that could provide the desired data on the quantity and quality of the dissolved or suspended pollutants in the waters of an industrial stream. Of the many approaches considered, the combination of solvent extraction followed by infrared spectroscopy of the extracts showed the greatest promise and was, therefore, developed further and became the routine method.

The specific infrared technique which we have found to be of greatest utility in the course of this two-year analytical program has been that of internal reflection spectroscopy. In this method a water sample or its solvent-extract, from the River itself, an industrial outfall or a City sewer line, is simply evaporated to dryness on a special plate about the size and shape of a microscope slide. Within a few minutes, the infrared spectrum can be scanned with no further sample handling required.

Figure 18 is a collection of infrared spectra resulting from evaporation of 50 ml aliquots of solutions of motor oil in a chlorinated solvent at concentrations ranging from 1 to 12 ppm, as recorded by the internal reflection technique. These spectra indicate the quality of the infrared "fingerprints" that can be obtained and the extraordinary sensitivity of the technique to oil present at concentrations in the ppm range.

Considering that, in generating the spectra collected in Figure 18, different internal reflection prisms were used, different standard solutions of the motor oil in the chlorinated solvent were prepared, the samples were analyzed on different days, and that there was a noticeable difference in the efficiency of distribution of the remnant samples during drying of the solvents, it is remarkable how reliable and regular are the increasing intensities of the absorption bands indicative of the presence of the hydrocarbon materials.

In the course of seeking a substitute for the hexane-extraction technique for hydrocarbons and oily pollutants in industrial waterways, a number of organic solvents were considered; the best of which and the most reliable of which was found to be chloroform. Figure 19 is a collection of infrared spectra illustrating the superiority of the chloroform extraction technique over the hexane extraction technique for both the qualitative and quantitative indication of hydrocarbon pollutants in water samples from the Buffalo River. As one studies the infrared spectra collected in Figure 19, it will be noted that there are three pairs of spectra obtained by both hexane and chloroform extraction of the identical water samples. Spectrum A at the top of



BASELINE FOR CLEAN GERMANIUM PRISM AS DETERMINED BY MULTIPLE ATTENUATED INTERNAL REFLECTION (MAIR) INFRARED SPECTROSCOPY

RESIDUE FROM SOLVENT BLANK

APPROXIMATELY 1 PPM MOTOR OIL

Figure 18 INFRARED SPECTRA RESULTING FROM EVAPORATION OF 50 ml ALIQUOTS OF SOLUTIONS OF MOTOR OIL IN A CHLORINATED SOLVENT, AT CONCENTRATIONS FROM 1 TO 12 PPM, AS RECORDED BY THE INTERNAL REFLECTION TECHNIQUE (SHEET 1 OF 2)

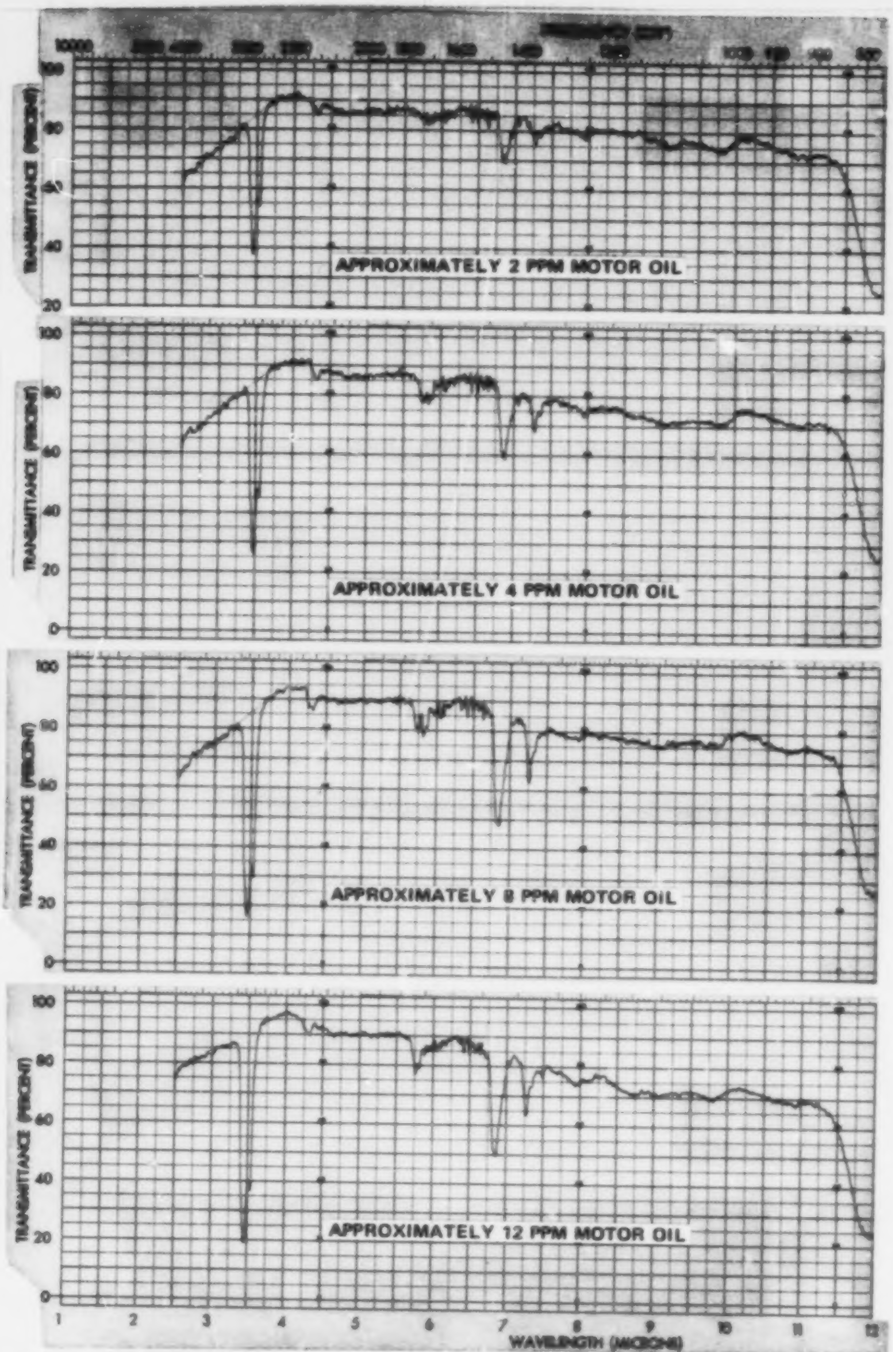


Figure 18 INFRARED SPECTRA RESULTING FROM EVAPORATION OF 50 ml ALIQUOTS OF SOLUTIONS OF MOTOR OIL IN A CHLORINATED SOLVENT, AT CONCENTRATIONS FROM 1 TO 12 PPM, AS RECORDED BY THE INTERNAL REFLECTION TECHNIQUE (SHEET 2 OF 2)

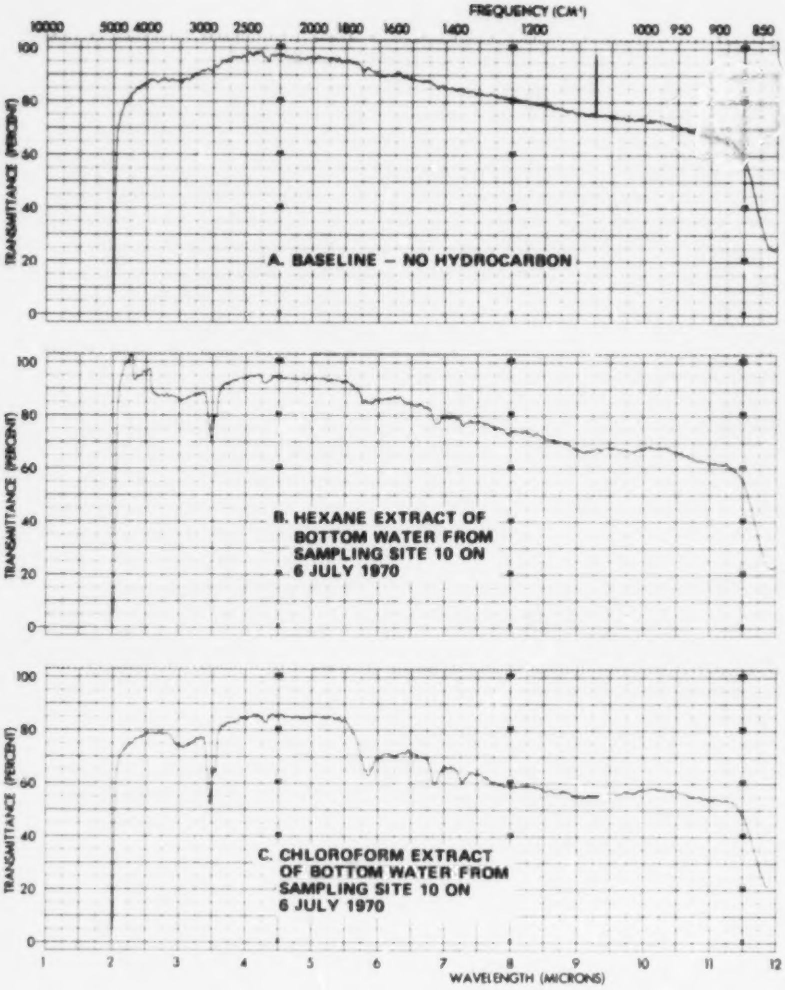


Figure 19 **INFRARED SPECTRA ILLUSTRATING SUPERIORITY OF CHLOROFORM-EXTRACTION TECHNIQUE OVER HEXANE-EXTRACTION TECHNIQUE FOR BOTH QUALITATIVE AND QUANTITATIVE ANALYSES OF "OILS" IN WATER SAMPLES FROM AN INDUSTRIAL WATERCOURSE (SHEET 1 OF 2)**

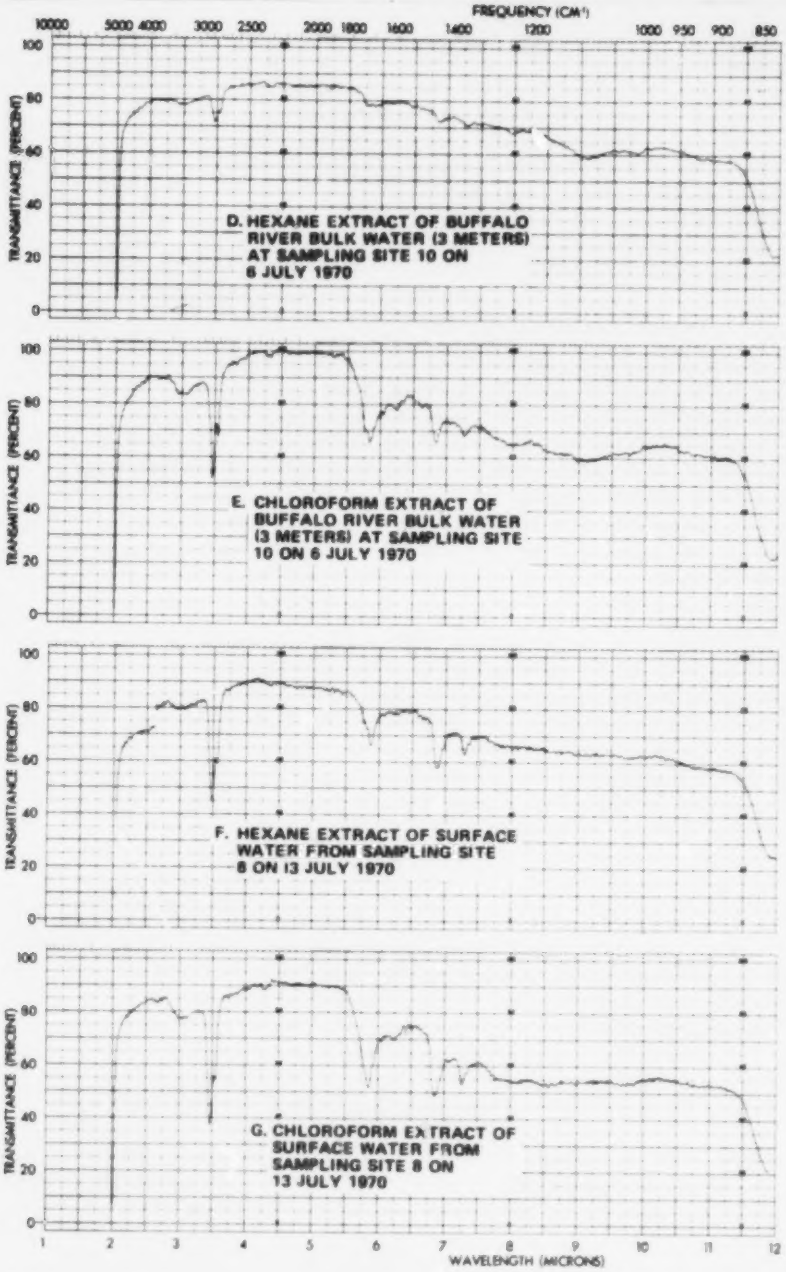


Figure 19 INFRARED SPECTRA ILLUSTRATING SUPERIORITY OF CHLOROFORM-EXTRACTION TECHNIQUE OVER HEXANE-EXTRACTION TECHNIQUE FOR BOTH QUALITATIVE AND QUANTITATIVE ANALYSES OF "OILS" IN WATER SAMPLES FROM AN INDUSTRIAL WATERCOURSE (SHEET 2 OF 2)

Figure 19 is the baseline against which all succeeding spectra should be judged. Traces B and C in Figure 19 represent, respectively, the residue from a hexane extract of bottom water from Site 10 in the Buffalo River (refer to Figure 2 for site locations) on July 6, 1970, and a chloroform extract from the same sample. Note the greater intensity of the hydrocarbon peaks in the chloroform extract, and also of the central peak at 1700 cm^{-1} indicative of the presence of oxygenated species. Traces D and E form a similar pair comparing the hexane extract of Buffalo River bulk water from a 3 meter depth at the same site and the chloroform extract of that water. Here, again, there is a striking difference in the amount of material actually selectively solubilized by the chloroform. The use of the chloroform extraction method, in preference to the hexane extraction method, has been especially successful for these bulk water samples. The final pair of traces, F and G, are, respectively, hexane and chloroform extracts of surface waters from Site 8 in the Buffalo River on July 13, 1970. They once again indicate the superiority of the chloroform extraction technique. Thus, taking water samples from the bottom through the mid-depth phases to the very hydrocarbon-enriched surface waters, the chloroform extraction method has been shown to give the best indication of the organic pollutants present, both qualitatively and quantitatively. Similar findings were made when extractions were made of collected oil slicks themselves, which were floating upon the water surface, and when examining sediments that had organic materials entrapped in them.

These comparative results were achieved during the 1970 sampling and analysis program and provided sufficient information to correct data taken in late 1968 (during the first sampling phase) and during the summer of 1969 when the hexane extraction technique was used exclusively on the bulk water samples. For example, water samples collected for our analysis in December of 1968 at twelve different locations on the Buffalo River, between its mouth and its confluence with Cazenovia Creek, when analyzed for total extractables by the hexane extraction method gave these results: the bulk water showed an average hexane extractable content of 20 ppm for industrial areas and approximately half that value for the non-industrial in the lower half of the Buffalo River. The bottom water samples were found to contain between 1 and 4% by weight of hexane extractables. It was noted in those analyses that many of the samples exhibited unknown interferences probably caused by organic dyes; the influence of these interferences could not be separated from the results given.

Over the course of the 1970 sampling and analysis program, regular comparisons made between the weights of chloroform-extractable matter and hexane-extractable matter in a variety of samples showed that there was usually a ratio of about two in favor of the hexane extracts. On first consideration, this appears to be a contradiction of the results given in Figure 19 in that the greater quantity of recovered material, by weight, was generally found in the hexane extract. The most likely explanation for this artifact was that, in the course of the hexane extraction technique and the gentle warming that is necessary to volatize the solvent without completely volatilizing the actual sample, a great deal of the normal aliphatic hexane remained entrapped with the oily residue. The quantitative weighing of the sample residue, therefore, led to a falsely inflated sample weight in the case of the hexane-extract. In recording the infrared spectra collected in Figure 19, it was certain that complete drying of the residues did take place. The observation documented in these spectra that the chloroform extraction did give both a greater quantity and variety of organic matter in the residue supports this interpretation of the hexane-induced artifact. Thus, the conclusion can be made that the values from hexane extracts of Buffalo River water samples for the 1968 and 1969 seasons were inflated by an approximate factor of two. Making this adjustment, it is found that the general quantity of "oil" suspended in the bulk waters of the Buffalo River was in the range around 5 to 10 ppm and not the higher value of some 20 ppm previously recorded. It should be added at this point, that it became necessary during the course of certain of the sample analyses, particularly those of the industrial outfalls whose natural pH values were on the basic side, to substitute as a solvent carbon tetrachloride for chloroform. In cross-correlation experiments of quantities extracted by chloroform vs carbon tetrachloride on identical samples of the Buffalo River water and of outfalls, it was always found that carbon tetrachloride extracted slightly less than the chloroform. Documentation of this gravimetric determination was confirmed by infrared spectroscopy.

A TYPICAL EXAMPLE OF THE SOLVENT EXTRACTION AND INFRARED ANALYSIS METHOD: COMPARISON OF CHLOROFORM EXTRACTION WITH CARBON TETRACHLORIDE EXTRACTION

Figure 20 contains infrared spectra showing results from carbon tetrachloride extraction of a Buffalo River water sample. The uppermost traces in Figure 20 represent the baseline and solvent "Blank." Carbon tetrachloride is a solvent that extracts predominantly non-polar hydrocarbons.

Figure 21 shows infrared spectra resulting from chloroform extracts of Buffalo River water. The uppermost traces in this Figure represent the baseline infrared spectra and solvent "Blank" for this test series. Chloroform is a powerful solvent that has the capability to solubilize both the polar and the non-polar oily pollutants, including suspended or emulsified globules of residual heavy fuel oils. An identical aliquot of Buffalo River bulk water was used in both extractions.

The experimental procedures followed for both extractions were identical. A sample volume of 100 ml of river water was mixed with a solvent volume of 50 ml and shaken vigorously in a chemical separatory funnel. A cloudy emulsion resulted. The emulsion was allowed to break slowly with the passage of time and the phases separated spontaneously into layered zones. The final appearance of the extracted phases for both solvents was the same. In each separatory funnel it was noted that

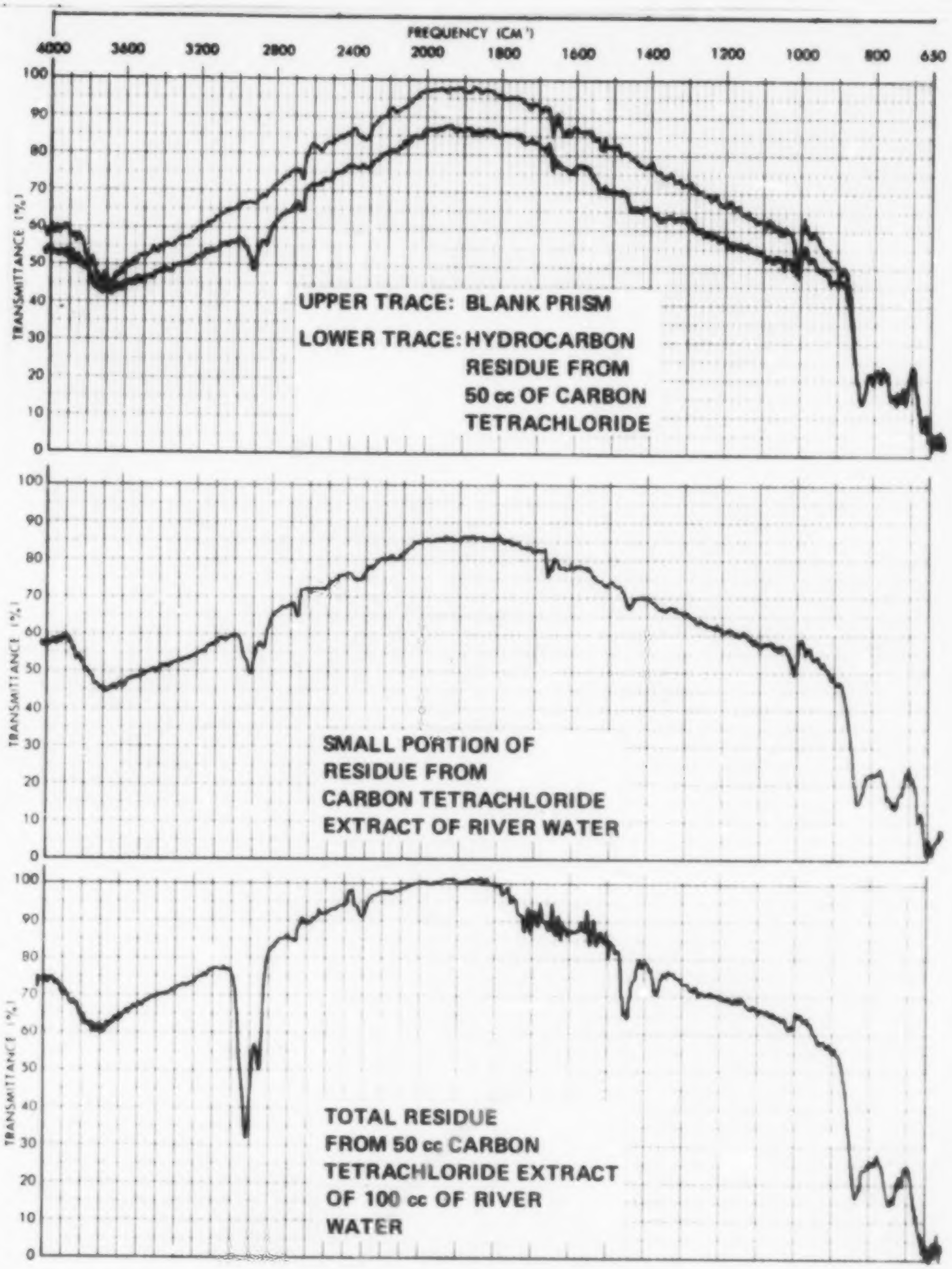


Figure 20 INFRARED SPECTRA SHOWING CARBON TETRACHLORIDE EXTRACTION METHOD FOR DETECTING NONPOLAR HYDROCARBON POLLUTANTS IN WATER

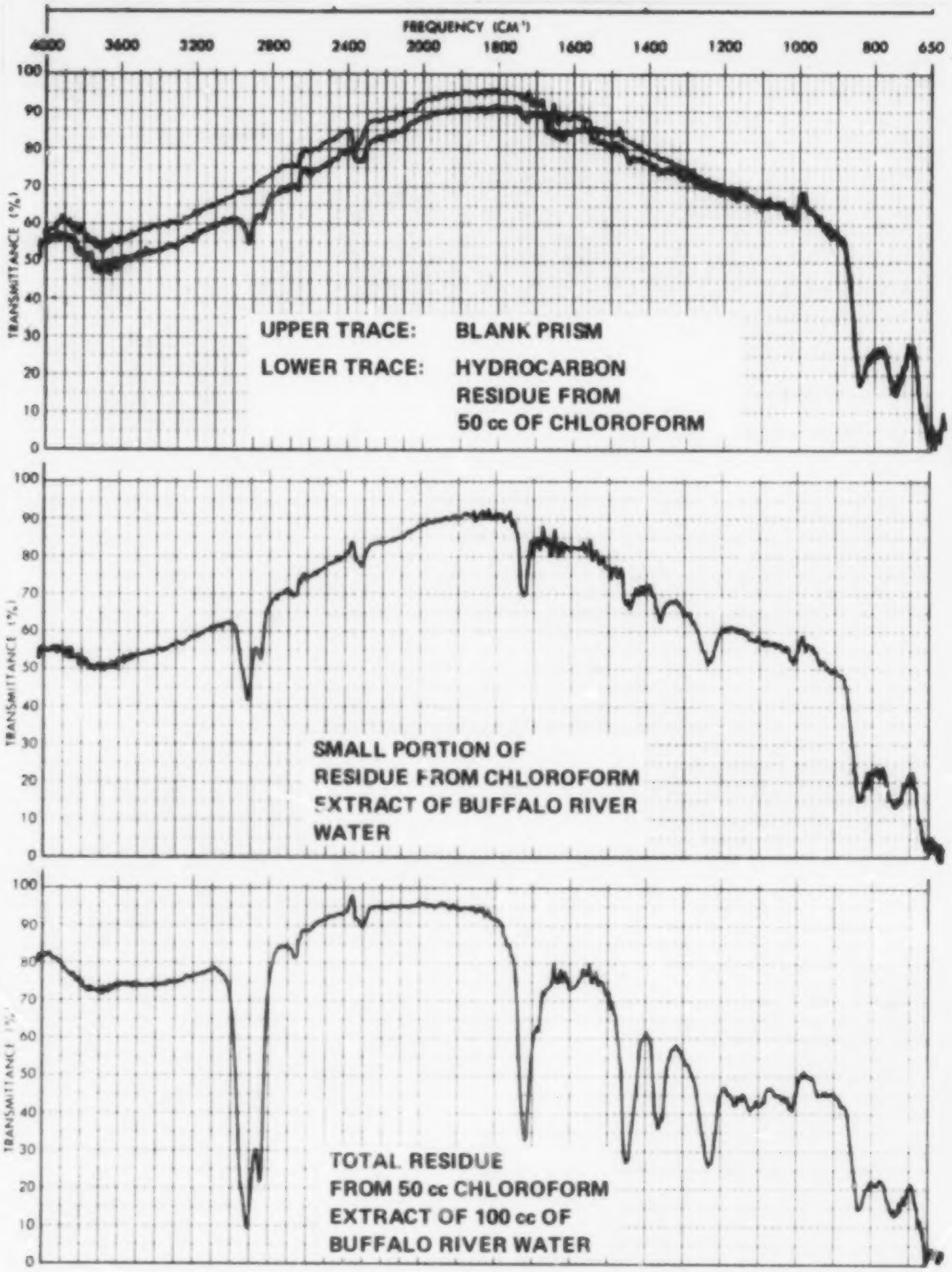


Figure 21 INFRARED SPECTRA SHOWING CHLOROFORM-EXTRACTION METHOD FOR DETECTING TOTAL HYDROCARBON LOAD (POLAR AND NONPOLAR) IN POLLUTED WATER

there was a bottom phase of about 50 ml of the solvent including the dissolved organic material extracted from the water. This bottom phase was separated from a clear upper phase of about 100 ml (the volume of the initial Buffalo River sample) by a narrow, dirty appearing middle phase of sediment. As a rapid qualitative check of the efficiency of the extractions and of their potential differences in character, a few drops of each bottom phase were routinely evaporated to dryness on a germanium internal reflection prism. The central traces in Figures 20 and 21 are the resulting infrared spectra of the residues from such spot samples. In Figure 20 one will note particularly the intensity of the hydrocarbon absorption band at 2900 cm^{-1} from a few droplets of the carbon tetrachloride which had intimately contacted the bulk river water. This intensity is about the same as the band resulting from the hydrocarbon residue carried by the whole 50 cc of the carbon tetrachloride before extraction, as is shown in the second trace in Figure 20. In Figure 21 the hydrocarbon absorption bands in the second trace (near 2900 cm^{-1} and 1360 cm^{-1}) for a few droplets of the pollution-loaded chloroform are shown. These bands are considerably more intense than those resulting from the dried residue of 50 cc of chloroform before its contact with the river water sample.

An important point to note here is that solvent "Blanks" of any of the solvents used in this investigation were never quite as free of extraneous hydrocarbons with grades of solvent less pure than "spectroscopic grade." Therefore, spectroscopy grade reagents were used throughout our investigation and are recommended for best use of the methods described here. Spectroscopy grade reagents are required especially for application to aqueous samples carrying minimal pollutant burdens.

Comparison of the lower traces in Figures 20 and 21 shows, further, that there is a substantial qualitative and quantitative difference in the materials extracted by the two chlorinated solvents. In addition to solvating the simple non-polar hydrocarbons, the chloroform also solvated the polar hydrocarbons that were originally dissolved or suspended in the river water. The infrared absorption bands at 1720 cm^{-1} and 1240 cm^{-1} are associated with carbonyl and carboxyl groups of the oxygenated polar hydrocarbons. Therefore, the total hydrocarbons present in an aqueous sample may be quantitatively estimated from a chloroform extract of a given volume of river water, and the relative quantities of polar and non-polar hydrocarbons making up this total may be obtained directly by comparison (for example, subtraction) of the amounts indicated in the spectrum obtained for the residue of a carbon tetrachloride extract of the same volume of the original sample. Figure 22 shows characteristic infrared spectra for the narrow middle phase present after extraction by carbon tetrachloride and chloroform. This figure demonstrates the essential absence of hydrocarbon bands in this dirty appearing middle phase. Rather, the spectra are dominated by the silica band at about 1000 cm^{-1} and show that this phase consists mainly of hydrocarbon-stripped inorganic sediment and thus may be safely ignored in the analytical scheme adopted for routine analysis.

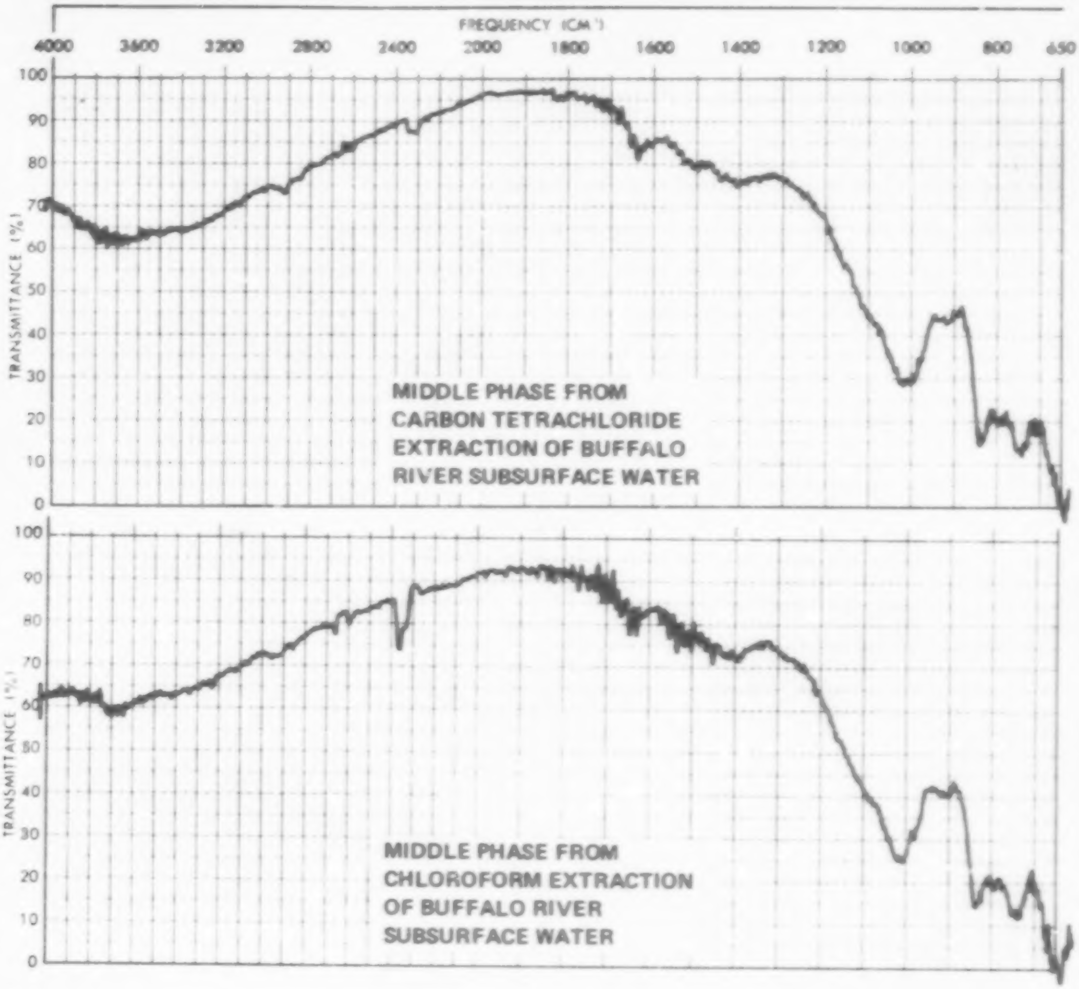


Figure 22 INFRARED SPECTRA CHARACTERIZING MIDDLE PHASE (SEDIMENT AND DIRT) FROM SOLVENT EXTRACTIONS OF BUFFALO RIVER WATER

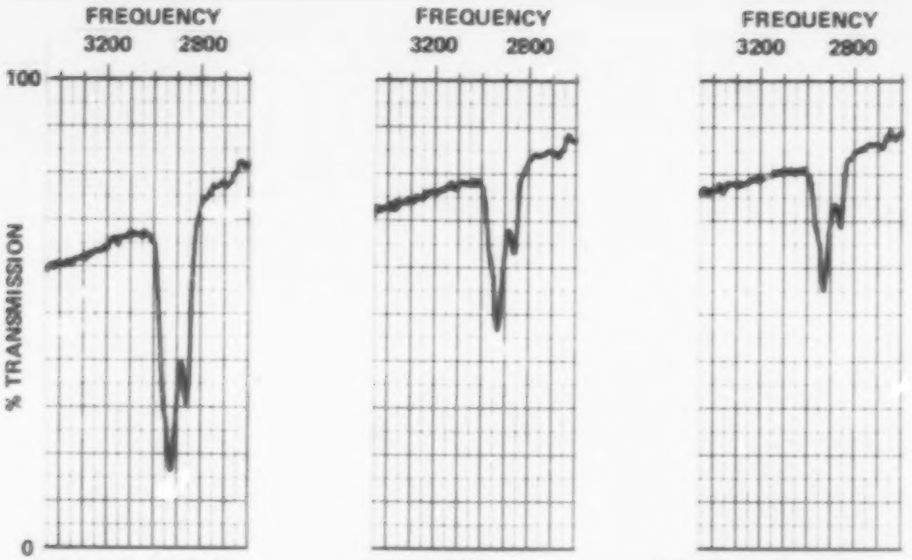
Since the internal reflection method is limited to thin films and small quantities of material, we also made regular routine use of the traditional transmission infrared techniques using defined aliquots of the solvent extracts in fixed-path cells to extend our quantification of the hydrocarbon load in all bulk samples and at all concentrations.

SPECIAL ANALYTICAL DETAILS

The exact analytical procedures, and particularly the use of various extraction solvents, varied somewhat from time to time. The bulk water samples, including water taken in a Kemmerer bottle at various depths, surface samples taken by the screen dip method, and one-inch surface water samples taken by the simple bag sampling technique, were routinely extracted using chloroform according to the slightly modified ASTM procedure outlined in Appendix B. Principal areas of departure from the ASTM method included shaking the sample in a separatory funnel rather than using a mechanical stirrer, and the substitution of a glass container in place of the platinum or silica evaporating dish specified in the standard for containing the desolvated extract. Samples of collected oil slicks obtained with the use of the surface-active sampling hoop, described earlier, were typically presented to the analyst as oil blots adsorbed to filter paper. These samples, which were normally sealed in small jars at the sampling point, were relatively straightforward to extract. An appropriate amount of chloroform was directly added to the sample and the jars tumbled on a ball mill or other suitable mechanical agitator. After this period, the chloroform was poured off through fat-free and oil-free special filter papers into a tared container. Another portion of chloroform was then added to the sample and a second extraction for a shorter time period was made to force the completeness of extraction. This solvent-plus-extracted-residue was filtered as before and combined with the previous extract in a glass container to allow desolvation at ambient temperature in a forced air stream.

A sequence of six samples of the oily pollutants found on the Buffalo River at six of the different sampling locations was shown in the SAMPLING section. These samples were retrieved semi-quantitatively on filter paper sheets using the surface-active hoop method. In addition to simple observation and weighing of the recovered samples, the extraction and analysis by infrared spectroscopy yielded the following results presented here as typical of the results achieved throughout the program in both the 1969 and 1970 seasons.

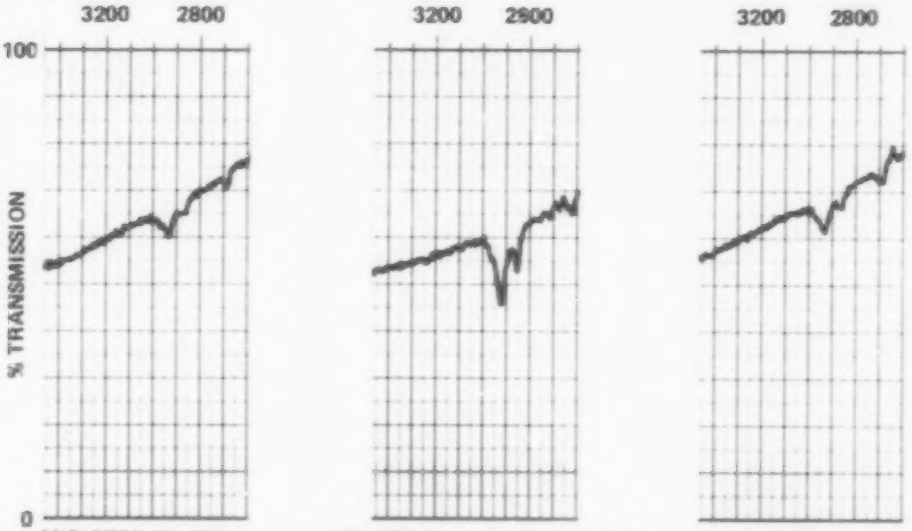
Figure 23 shows the spectrum of each of the six samples in a selected part of the infrared region which includes the major oil absorption band. These spectra were obtained by simple extraction of each oil loaded filter paper (each filter paper representing the oil pollution over a confined and known surface area) according to the procedure just outlined and then depositing a known amount of each extract on germanium internal reflection prisms. The spectra show quite directly the relatively large amount of pollution at the natural trap near the South Park



NATURAL TRAP AT SOUTH PARK BRIDGE

MID-STREAM AT SOUTH PARK BRIDGE

MID-STREAM NEAR NATIONAL ANILINE PLANT



MID-STREAM NEAR MOBIL OIL PLANT

MID-STREAM AT MICHIGAN AVENUE LIFT BRIDGE (AIR BARRIER OPERATING)

IN CURRENT FROM AIR BARRIER

NOTE: RELATIVE BAND INTENSITY CORRELATES WITH QUANTITY OF POLLUTION PRESENT AT EACH SITE.

Figure 23 OIL ABSORPTION BANDS IN THE INFRARED SPECTRA OF CHLOROFORM EXTRACTS OF HOOP-SAMPLES AT VARIOUS LOCATIONS IN THE BUFFALO RIVER

Bridge compared to other sites upstream and downstream from South Park Avenue. The intensity of the absorption bands was correlated directly with the quantity of oil present at each location and was also qualitatively indicated in the earlier figure by the visual appearance of such samples on the filter papers.

The industrial outfall samples collected during this program were extracted in a somewhat milder manner: after recording the pH of the samples, acidification before extraction was not conducted. In the case of the outfall samples, the extraction solvent was selected on the basis of the recorded pH. Throughout this effort, chloroform was used as the extraction solvent of preference due to its already noted high solvent power for oily pollutants and its known low water solubility. This solvent was unsuitable for use in the extraction of industrial discharges whose pH was naturally on the basic side. This elimination of our favored solvent was prompted by the possible base-catalyzed formation of the highly reactive carbene species, $:CCl_2$ (Reference 1). To circumvent this problem without modifying the sample pH, and thereby changing the chemical nature of the polluting constituents or perhaps precipitating some of them from the material, the carbon tetrachloride solvent was used for the extraction in all outfall samples having a pH above 8.0. Therefore, for these samples of industrial outfalls, the indicated quantities of entrained oily pollutants recorded in later sections of this report must be considered to be on the low side since it is known that the carbon tetrachloride was not capable of solvating many of the polar constituents.

The River bottom sediments were analyzed for chloroform extractable material by the following procedure: a typical sediment or mud sample was submitted to the analyst in a glass jar containing about 1 kg of material. Before removing a smaller sample for actual analysis, the entire original sample was thoroughly agitated to achieve distributive homogeneity of the material. A portion of the homogenized mass was then weighed to the nearest tenth gram and then quantitatively transferred to a blender with about 100 ml of distilled water. Then 50 ml of the chloroform was added and the slurry agitated at a slow speed for five minutes. The resultant solvent-extracted slurry was then quantitatively transferred to a Buchner funnel with No. 31 Whatman paper in place. Filtering took place at a reduced pressure into a one liter vacuum filter flask. The filter cake was subsequently washed three times with 50 ml portions of fresh chloroform. The filtrate was then transferred to a suitable separatory funnel, rinsing the flask with more fresh chloroform. The separated chloroform was finally transferred into a tared glass container for desolvation with an ambient temperature air stream.

The analysis of samples using the instrumental methods and using electromagnetic radiation of various wavelengths proceeded by standard techniques familiar to most analytical groups and therefore will not be described in greater detail in this report.

CHARACTERIZATION OF THE POLLUTANT BURDEN IN THE BULK WATERS OF THE BUFFALO RIVER

The following compilation of data, which is very extensive and includes information from as far back as 1964, has been gathered with the assistance and cooperation of the following parties in addition to Cornell Aeronautical Laboratory personnel. We are grateful to Mr. John S. Tygert of the New York State Environmental Conservation Department for forwarding average data from the 1964 survey project on the Buffalo River. These data were reduced in the offices of the Department of Health, Education, and Welfare, Public Health Service, Great Lakes River Basins project headquartered in Cleveland, Ohio. The information was forwarded to the Buffalo Regional Office by Charles W. Northington, Director of the Lake Erie Program Office. We are also grateful to Dr. Robert Sweeney, Director of the Great Lakes Laboratory of the State University College of New York at Buffalo, for providing certain data also included in this compilation. We are further in the debt of Mr. Richard A. Kressin, Chemist at the Buffalo Sewer Authority, Sewage Treatment Works, for forwarding results of the comprehensive surveys which his group conducted on the Buffalo River during the 1970 season.

Figures 24 through 41 present typical analytical results characterizing the Buffalo River along its entire length (as defined in the introduction to this report) for the years 1964, 1968, 1969, and 1970. The year 1964 represents the general condition of the River for the years prior to the introduction of the Buffalo River cooling water project (Buffalo River Improvement Project). The 1968, 1969 and 1970 compilations represent contributions made during the performance period of the present EPA funded program, after initiation of the cooling water project. It will be recognized that Figures 24 through 41 are, simplified, richly annotated versions of the Buffalo River plan view which was presented in the introductory section as Figure 2. Figures presented here provide only an overview of the quality of the River over the periods described and present in a comprehensive fashion the summation of data available characterizing this industrial waterway as it changed during the past eight years. It will be noted on inspection of these figures that there is information provided on analysis of river bottom sediments, oil content at various depths in the River and along its entire length, the bacterial load in terms of coliforms and fecal coliforms found in the River, and meteorological conditions prevailing during sampling. The complete body of data from which these Figures have been abstracted, and a similar collection of Figures for numerous other sampling dates, are retained in the files of Cornell Aeronautical Laboratory for the inspection of other water pollution control researchers who might attempt an interpretive analysis in greater detail than that warranted in this report.

A brief summation and interpretation of the extensive amount of information acquired about this typical watercourse is in order, however.

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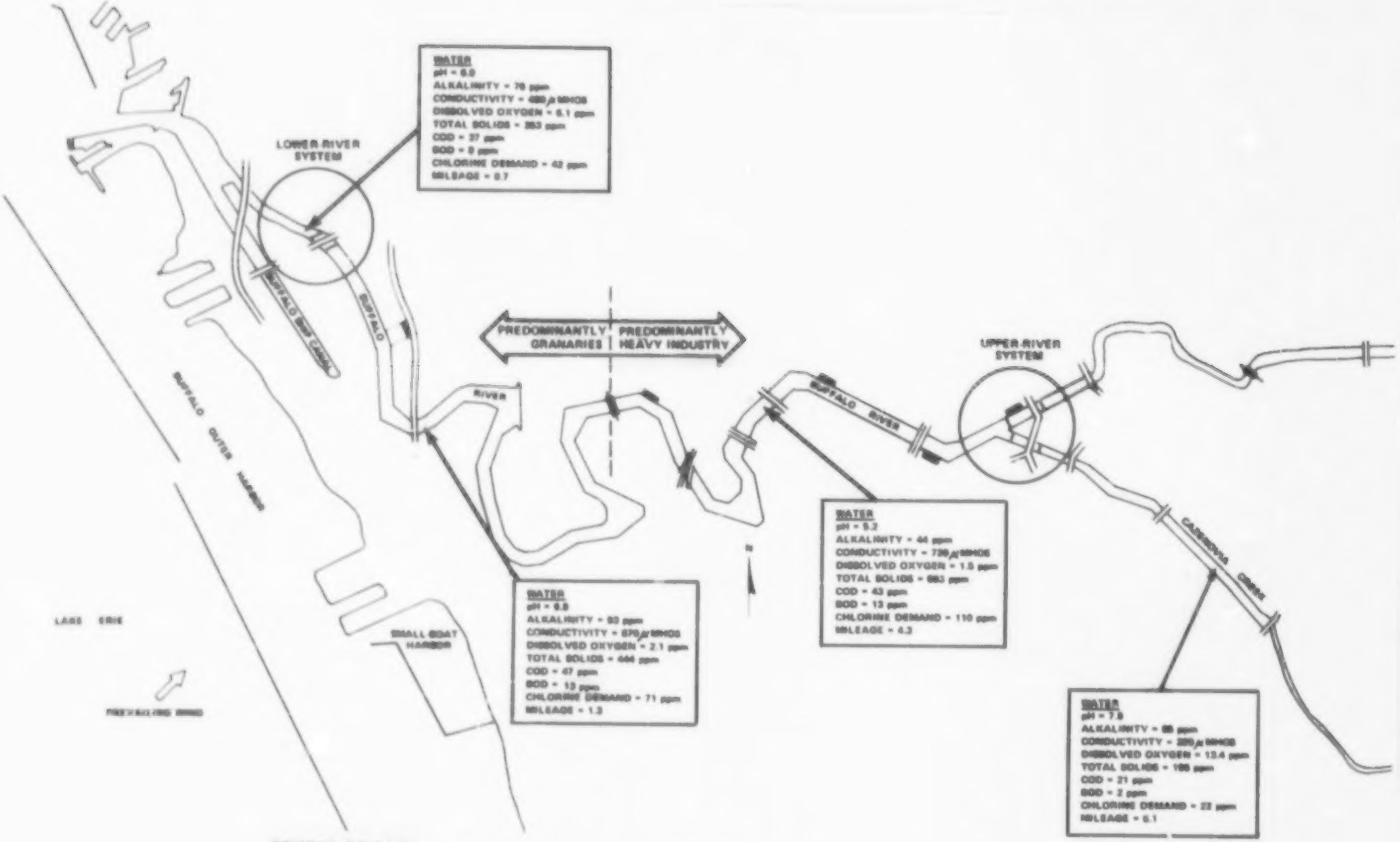
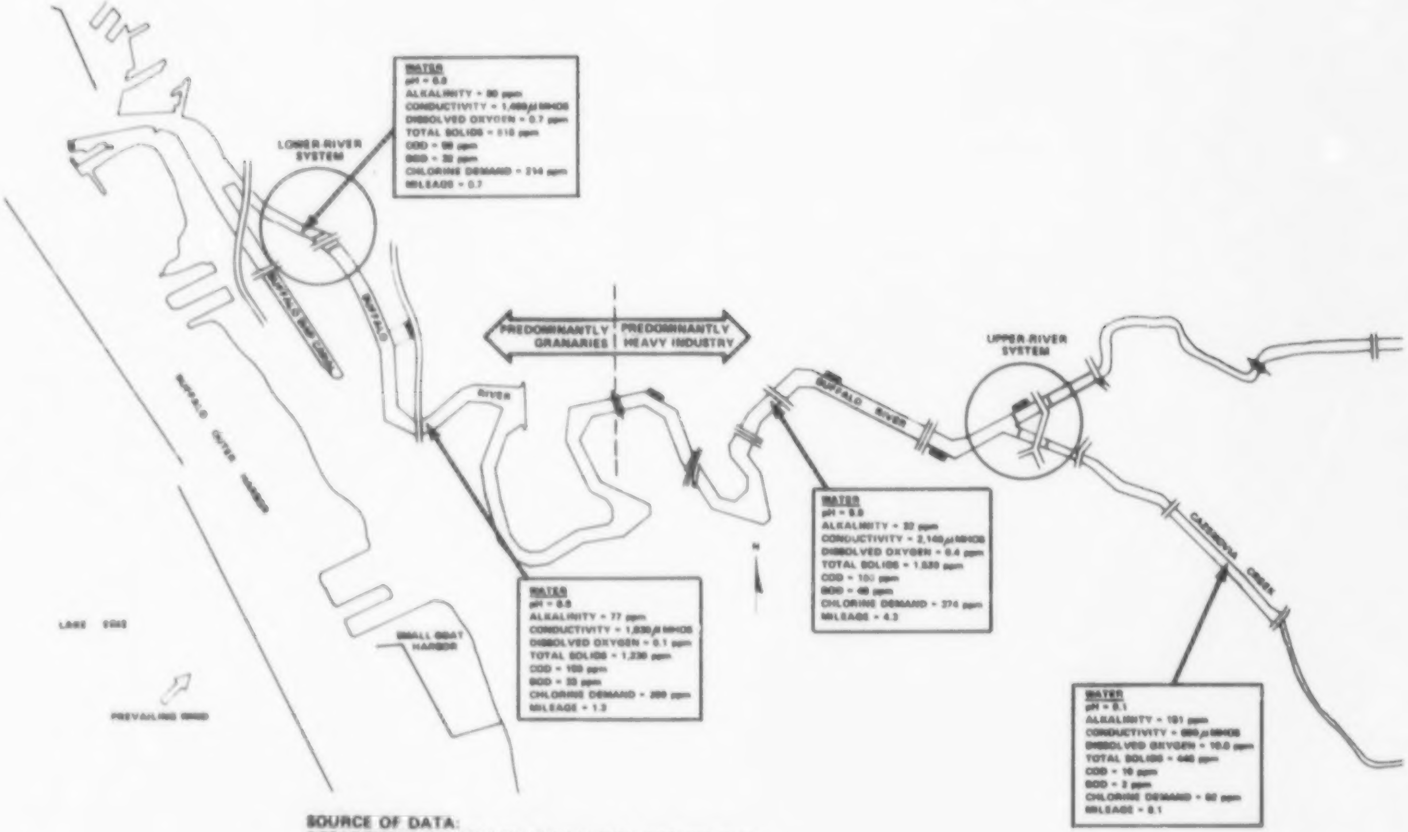

LOWER RIVER SYSTEM
WATER
pH = 6.9
ALKALINITY = 76 ppm
CONDUCTIVITY = 480 µ MHOS
DISSOLVED OXYGEN = 5.1 ppm
TOTAL SOLIDS = 353 ppm
COD = 37 ppm
BOD = 9 ppm
CHLORINE DEMAND = 42 ppm
MILEAGE = 0.7
BUFFALO SHIP CANAL
BUFFALO
RIVER
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
UPPER RIVER SYSTEM
BUFFALO RIVER
CAZENOVIA CREEK
BUFFALO OUTER HARBOR
LAKE ERIE
PREVAILING WIND
SMALL BOAT HARBOR
N
WATER
pH = 6.8
ALKALINITY = 93 ppm
CONDUCTIVITY = 570 µ MHOS
DISSOLVED OXYGEN = 2.1 ppm
TOTAL SOLIDS = 444 ppm
COD = 47 ppm
BOD = 13 ppm
CHLORINE DEMAND = 71 ppm
MILEAGE = 1.3
WATER
pH = 5.2
ALKALINITY = 44 ppm
CONDUCTIVITY = 730 µ MHOS
DISSOLVED OXYGEN = 1.5 ppm
TOTAL SOLIDS = 663 ppm
COD = 43 ppm
BOD = 13 ppm
CHLORINE DEMAND = 110 ppm
MILEAGE = 4.3
WATER
pH = 7.8
ALKALINITY = 85 ppm
CONDUCTIVITY = 220 µ MHOS
DISSOLVED OXYGEN = 13.4 ppm
TOTAL SOLIDS = 166 ppm
COD = 21 ppm
BOD = 2 ppm
CHLORINE DEMAND = 22 ppm
MILEAGE = 6.1

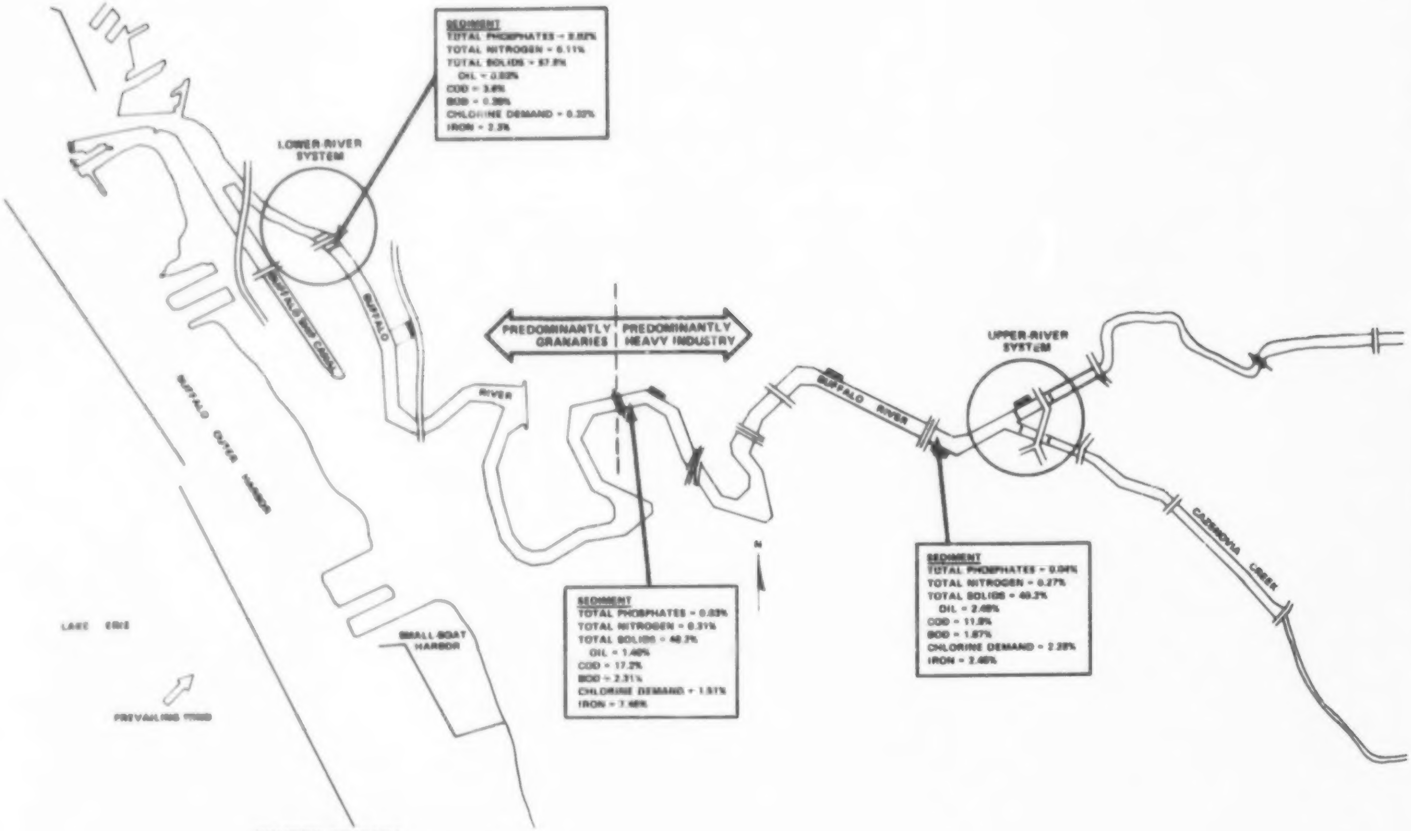
SOURCE OF DATA:
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Figure 24 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR PERIOD 1 APRIL 1964 THROUGH 30 MAY 1964


WATER
pH = 6.8
ALKALINITY = 80 ppm
CONDUCTIVITY = 1,480 µMHOS
DISSOLVED OXYGEN = 0.7 ppm
TOTAL SOLIDS = 810 ppm
COD = 96 ppm
BOD = 32 ppm
CHLORINE DEMAND = 214 ppm
MILEAGE = 0.7
LOWER RIVER SYSTEM
BUFFALO SHIP CANAL
BUFFALO
RIVER
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO OUTER HARBOR
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND
WATER
pH = 6.8
ALKALINITY = 77 ppm
CONDUCTIVITY = 1,830 µMHOS
DISSOLVED OXYGEN = 0.1 ppm
TOTAL SOLIDS = 1,230 ppm
COD = 100 ppm
BOD = 30 ppm
CHLORINE DEMAND = 280 ppm
MILEAGE = 1.3
N
BUFFALO RIVER
WATER
pH = 6.9
ALKALINITY = 32 ppm
CONDUCTIVITY = 2,140 µMHOS
DISSOLVED OXYGEN = 0.4 ppm
TOTAL SOLIDS = 1,530 ppm
COD = 100 ppm
BOD = 48 ppm
CHLORINE DEMAND = 274 ppm
MILEAGE = 4.3
UPPER RIVER SYSTEM
CAZENOVIA CREEK
WATER
pH = 8.1
ALKALINITY = 101 ppm
CONDUCTIVITY = 680 µMHOS
DISSOLVED OXYGEN = 10.0 ppm
TOTAL SOLIDS = 440 ppm
COD = 16 ppm
BOD = 2 ppm
CHLORINE DEMAND = 60 ppm
MILEAGE = 8.1

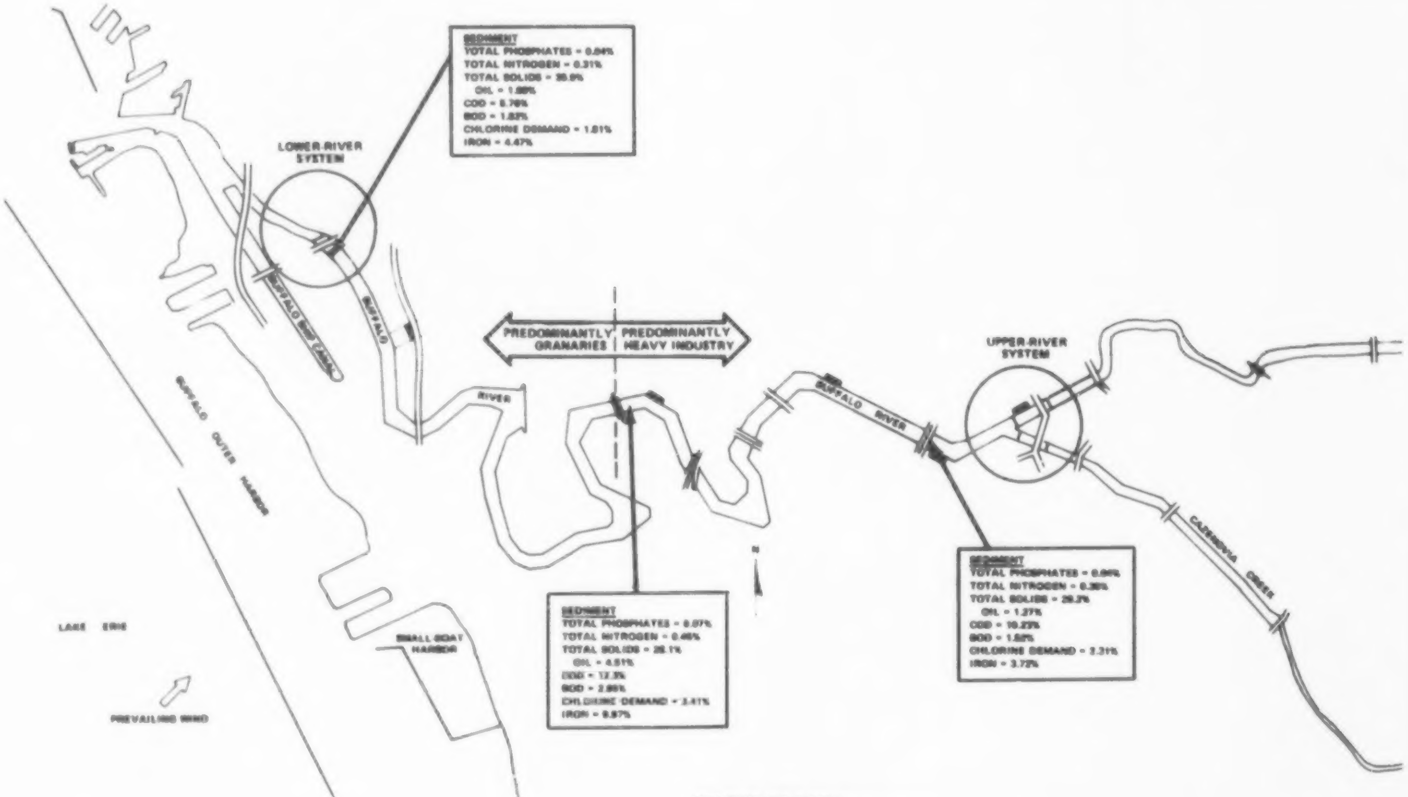
SOURCE OF DATA:
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Figure 25 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR PERIOD 1 OCTOBER 1964 THROUGH 30 NOVEMBER 1964


SEDIMENT
TOTAL PHOSPHATES = 0.02%
TOTAL NITROGEN = 0.11%
TOTAL SOLIDS = 57.8%
OIL = 0.03%
COD = 3.6%
BOD = 0.38%
CHLORINE DEMAND = 0.32%
IRON = 2.3%
LOWER-RIVER SYSTEM
BUFFALO SHIP CANAL
BUFFALO
RIVER
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO OUTER HARBOR
LAKE ERIE
PREVAILING WIND
SMALL BOAT HARBOR
N
SEDIMENT
TOTAL PHOSPHATES = 0.03%
TOTAL NITROGEN = 0.31%
TOTAL SOLIDS = 48.7%
OIL = 1.40%
COD = 17.2%
BOD = 2.31%
CHLORINE DEMAND = 1.51%
IRON = 7.48%
BUFFALO RIVER
UPPER-RIVER SYSTEM
SEDIMENT
TOTAL PHOSPHATES = 0.04%
TOTAL NITROGEN = 0.27%
TOTAL SOLIDS = 49.2%
OIL = 2.48%
COD = 11.8%
BOD = 1.87%
CHLORINE DEMAND = 2.28%
IRON = 2.48%
CAZENOVIA CREEK

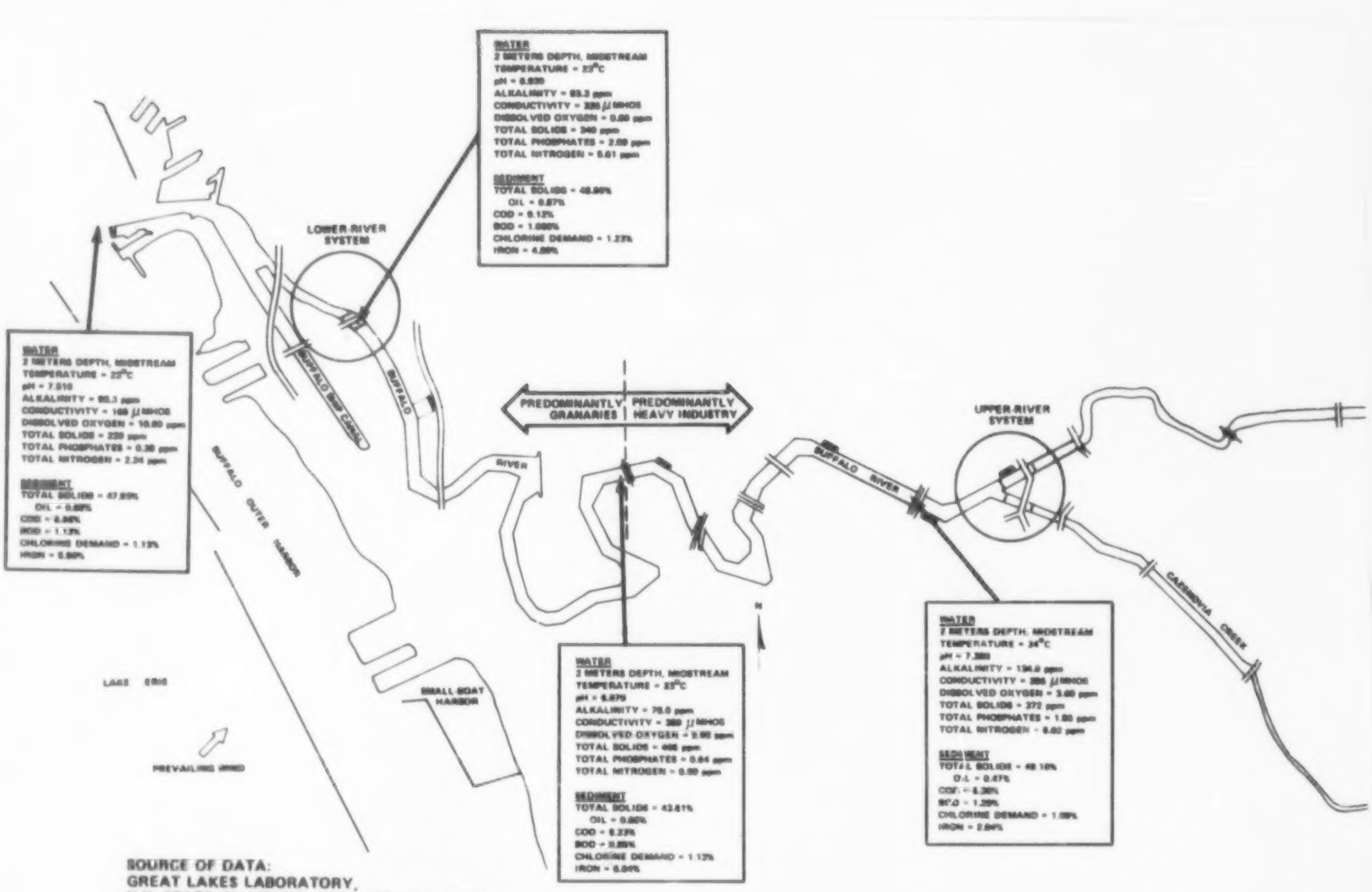
SOURCE OF DATA:
GREAT LAKES LABORATORY,
N.Y. STATE UNIVERSITY COLLEGE AT BUFFALO

Figure 26 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 19 JUNE 1968 (BEFORE DREDGING OF HARBOR AREA)


SEDIMENT
TOTAL PHOSPHATES = 0.04%
TOTAL NITROGEN = 0.31%
TOTAL SOLIDS = 35.0%
OIL = 1.88%
COD = 5.76%
BOD = 1.82%
CHLORINE DEMAND = 1.01%
IRON = 4.47%
LOWER-RIVER SYSTEM
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
UPPER-RIVER SYSTEM
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO RIVER
CAZENOVIA CREEK
BUFFALO OUTER HARBOR
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND
N
SEDIMENT
TOTAL PHOSPHATES = 0.07%
TOTAL NITROGEN = 0.46%
TOTAL SOLIDS = 28.1%
OIL = 4.51%
COD = 12.3%
BOD = 2.85%
CHLORINE DEMAND = 3.41%
IRON = 9.87%
SEDIMENT
TOTAL PHOSPHATES = 0.06%
TOTAL NITROGEN = 0.30%
TOTAL SOLIDS = 26.2%
OIL = 1.27%
COD = 10.23%
BOD = 1.52%
CHLORINE DEMAND = 2.31%
IRON = 3.72%

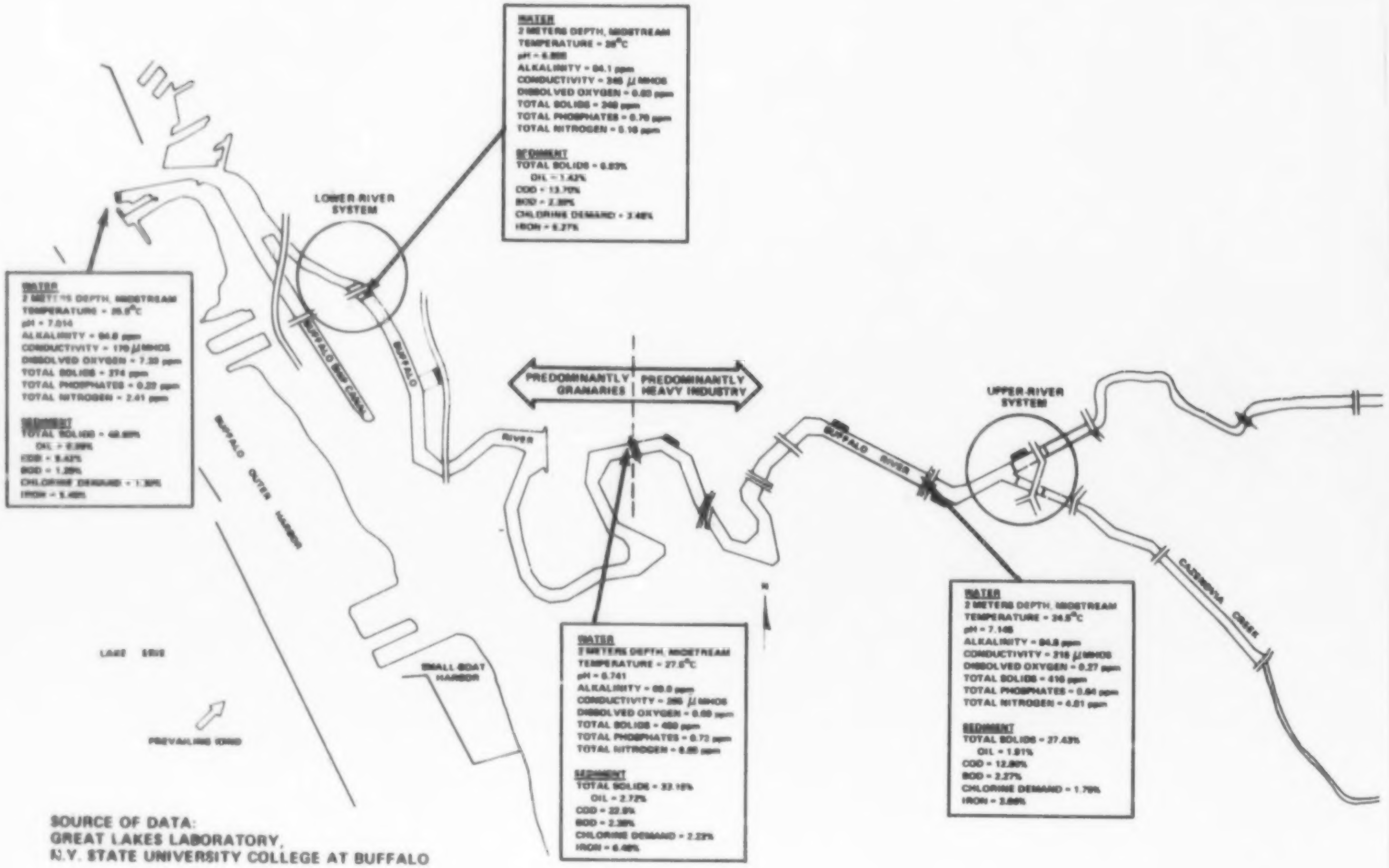
SOURCE OF DATA:
GREAT LAKES LABORATORY,
N.Y. STATE UNIVERSITY COLLEGE AT BUFFALO

Figure 27 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 17 OCTOBER 1968 (AFTER DREDGING OF HARBOR AREA)


WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 23°C
pH = 6.930
ALKALINITY = 83.3 ppm
CONDUCTIVITY = 320 μ MHOS
DISSOLVED OXYGEN = 0.80 ppm
TOTAL SOLIDS = 340 ppm
TOTAL PHOSPHATES = 2.00 ppm
TOTAL NITROGEN = 5.61 ppm
SEDIMENT
TOTAL SOLIDS = 48.90%
OIL = 0.87%
COD = 9.12%
BOD = 1.080%
CHLORINE DEMAND = 1.27%
IRON = 4.88%
LOWER RIVER SYSTEM
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 22°C
pH = 7.510
ALKALINITY = 93.3 ppm
CONDUCTIVITY = 169 μ MHOS
DISSOLVED OXYGEN = 10.80 ppm
TOTAL SOLIDS = 220 ppm
TOTAL PHOSPHATES = 0.30 ppm
TOTAL NITROGEN = 2.24 ppm
SEDIMENT
TOTAL SOLIDS = 47.29%
OIL = 0.88%
COD = 6.96%
BOD = 1.13%
CHLORINE DEMAND = 1.13%
IRON = 5.90%
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO OUTER HARBOR
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
UPPER RIVER SYSTEM
BUFFALO RIVER
CAZENOVIA CREEK
N
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 23°C
pH = 6.870
ALKALINITY = 78.0 ppm
CONDUCTIVITY = 280 μ MHOS
DISSOLVED OXYGEN = 0.90 ppm
TOTAL SOLIDS = 466 ppm
TOTAL PHOSPHATES = 0.64 ppm
TOTAL NITROGEN = 0.80 ppm
SEDIMENT
TOTAL SOLIDS = 43.61%
OIL = 0.86%
COD = 8.22%
BOD = 0.89%
CHLORINE DEMAND = 1.13%
IRON = 6.04%
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 24°C
pH = 7.380
ALKALINITY = 134.0 ppm
CONDUCTIVITY = 286 μ MHOS
DISSOLVED OXYGEN = 3.60 ppm
TOTAL SOLIDS = 372 ppm
TOTAL PHOSPHATES = 1.86 ppm
TOTAL NITROGEN = 6.02 ppm
SEDIMENT
TOTAL SOLIDS = 48.10%
OIL = 0.47%
COD = 6.30%
BOD = 1.29%
CHLORINE DEMAND = 1.09%
IRON = 2.04%

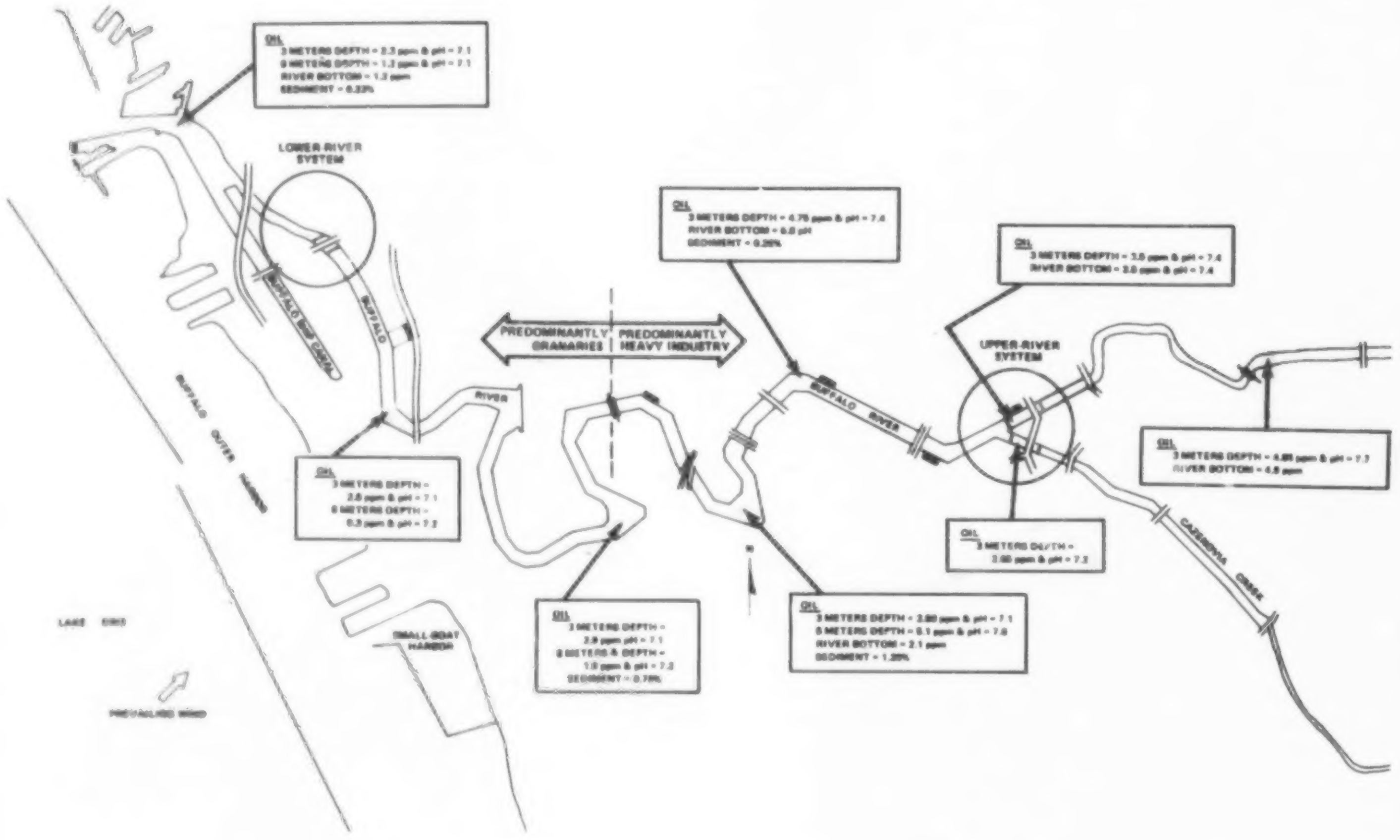
SOURCE OF DATA:
GREAT LAKES LABORATORY,
N.Y. STATE UNIVERSITY COLLEGE AT BUFFALO

Figure 28 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 2 JUNE 1969


WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 25.5°C
pH = 7.014
ALKALINITY = 94.8 ppm
CONDUCTIVITY = 170 µMHOS
DISSOLVED OXYGEN = 7.30 ppm
TOTAL SOLIDS = 274 ppm
TOTAL PHOSPHATES = 0.22 ppm
TOTAL NITROGEN = 2.41 ppm
SEDIMENT
TOTAL SOLIDS = 48.80%
OIL = 0.99%
COD = 8.42%
BOD = 1.29%
CHLORINE DEMAND = 1.30%
IRON = 5.40%
LOWER RIVER SYSTEM
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 26°C
pH = 6.888
ALKALINITY = 94.1 ppm
CONDUCTIVITY = 346 µMHOS
DISSOLVED OXYGEN = 0.60 ppm
TOTAL SOLIDS = 240 ppm
TOTAL PHOSPHATES = 0.70 ppm
TOTAL NITROGEN = 5.16 ppm
SEDIMENT
TOTAL SOLIDS = 6.83%
OIL = 1.42%
COD = 13.70%
BOD = 2.30%
CHLORINE DEMAND = 3.48%
IRON = 5.27%
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO OUTER HARBOR
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO RIVER
UPPER RIVER SYSTEM
CAZENOVIA CREEK
N
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 27.5°C
pH = 6.741
ALKALINITY = 88.0 ppm
CONDUCTIVITY = 295 µMHOS
DISSOLVED OXYGEN = 0.60 ppm
TOTAL SOLIDS = 460 ppm
TOTAL PHOSPHATES = 0.72 ppm
TOTAL NITROGEN = 6.86 ppm
SEDIMENT
TOTAL SOLIDS = 33.18%
OIL = 2.72%
COD = 22.9%
BOD = 2.38%
CHLORINE DEMAND = 2.22%
IRON = 6.48%
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 24.5°C
pH = 7.148
ALKALINITY = 94.8 ppm
CONDUCTIVITY = 318 µMHOS
DISSOLVED OXYGEN = 0.27 ppm
TOTAL SOLIDS = 416 ppm
TOTAL PHOSPHATES = 0.64 ppm
TOTAL NITROGEN = 4.81 ppm
SEDIMENT
TOTAL SOLIDS = 27.43%
OIL = 1.91%
COD = 12.80%
BOD = 2.27%
CHLORINE DEMAND = 1.79%
IRON = 2.88%
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND

SOURCE OF DATA:
GREAT LAKES LABORATORY,
N.Y. STATE UNIVERSITY COLLEGE AT BUFFALO

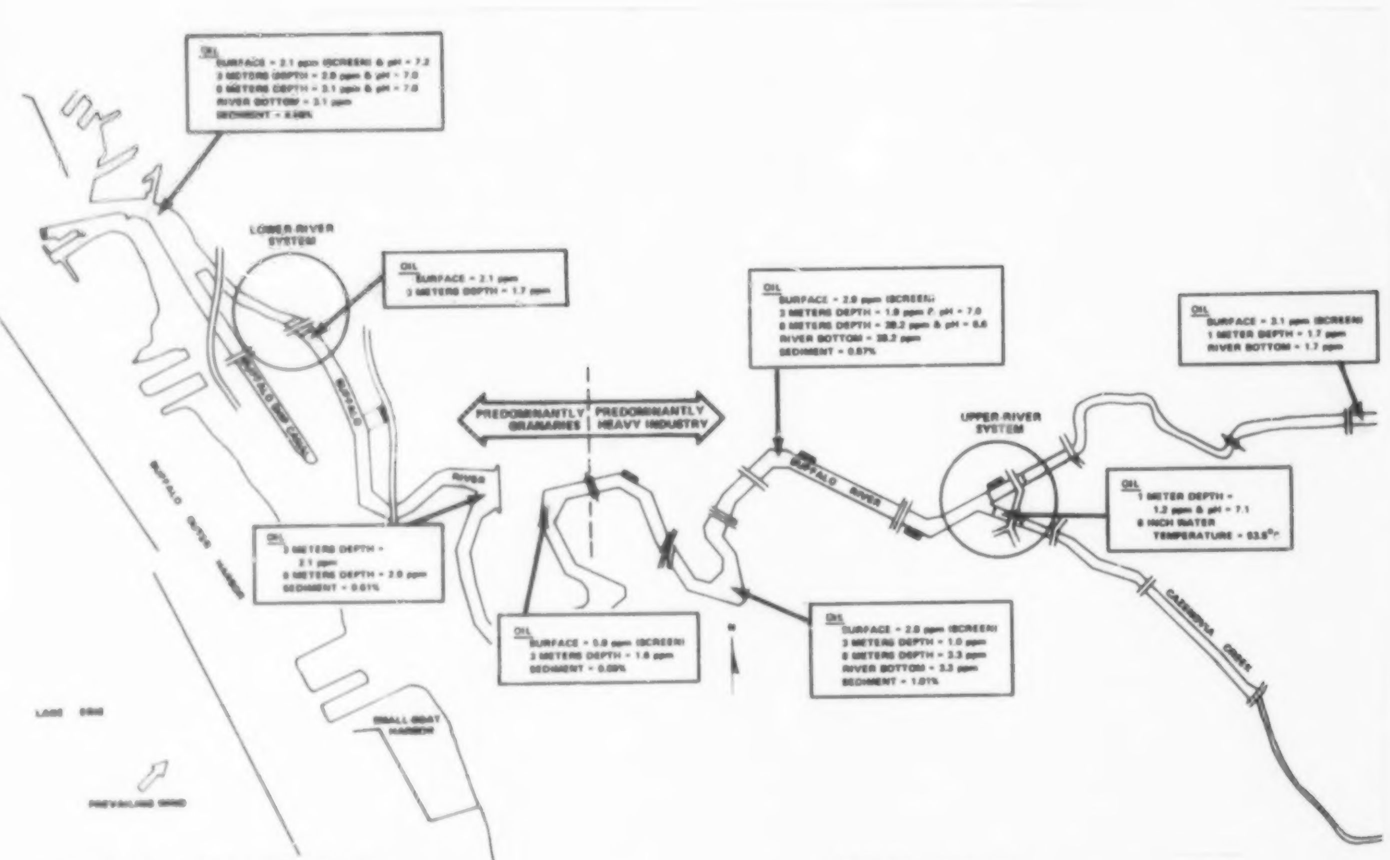
Figure 29 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 22 SEPTEMBER 1969


OIL
3 METERS DEPTH = 2.3 ppm & pH = 7.1
6 METERS DEPTH = 1.2 ppm & pH = 7.1
RIVER BOTTOM = 1.2 ppm
SEDIMENT = 0.23%
LOWER RIVER SYSTEM
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO OUTER HARBOR
OIL
3 METERS DEPTH = 2.8 ppm & pH = 7.1
6 METERS DEPTH = 0.3 ppm & pH = 7.2
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
OIL
3 METERS DEPTH = 4.75 ppm & pH = 7.4
RIVER BOTTOM = 6.0 pH
SEDIMENT = 0.26%
OIL
3 METERS DEPTH = 3.0 ppm & pH = 7.4
RIVER BOTTOM = 3.0 ppm & pH = 7.4
UPPER-RIVER SYSTEM
BUFFALO RIVER
OIL
3 METERS DEPTH = 4.85 ppm & pH = 7.7
RIVER BOTTOM = 4.8 ppm
OIL
3 METERS DEPTH = 2.60 ppm & pH = 7.2
CAZENOVIA CREEK
N
OIL
3 METERS DEPTH = 2.80 ppm & pH = 7.1
6 METERS DEPTH = 5.1 ppm & pH = 7.8
RIVER BOTTOM = 2.1 ppm
SEDIMENT = 1.28%
OIL
3 METERS DEPTH = 2.9 ppm pH = 7.1
6 METERS & DEPTH = 1.0 ppm & pH = 7.2
SEDIMENT = 0.78%
LAKE ERIE
PREVAILING WIND
SMALL BOAT HARBOR

WEATHER: 2nd BRIGHT SUNNY DAY IN A ROW
WIND DIR.: WNW @ ≈10 mph
TEMPERATURE = 70°F; RELATIVE HUMIDITY = 31%
ATMOSPHERIC PRESSURE = 28.92 in.

SOURCES OF DATA:
CORNELL AERONAUTICAL LABORATORY
AND BUFFALO SEWER AUTHORITY

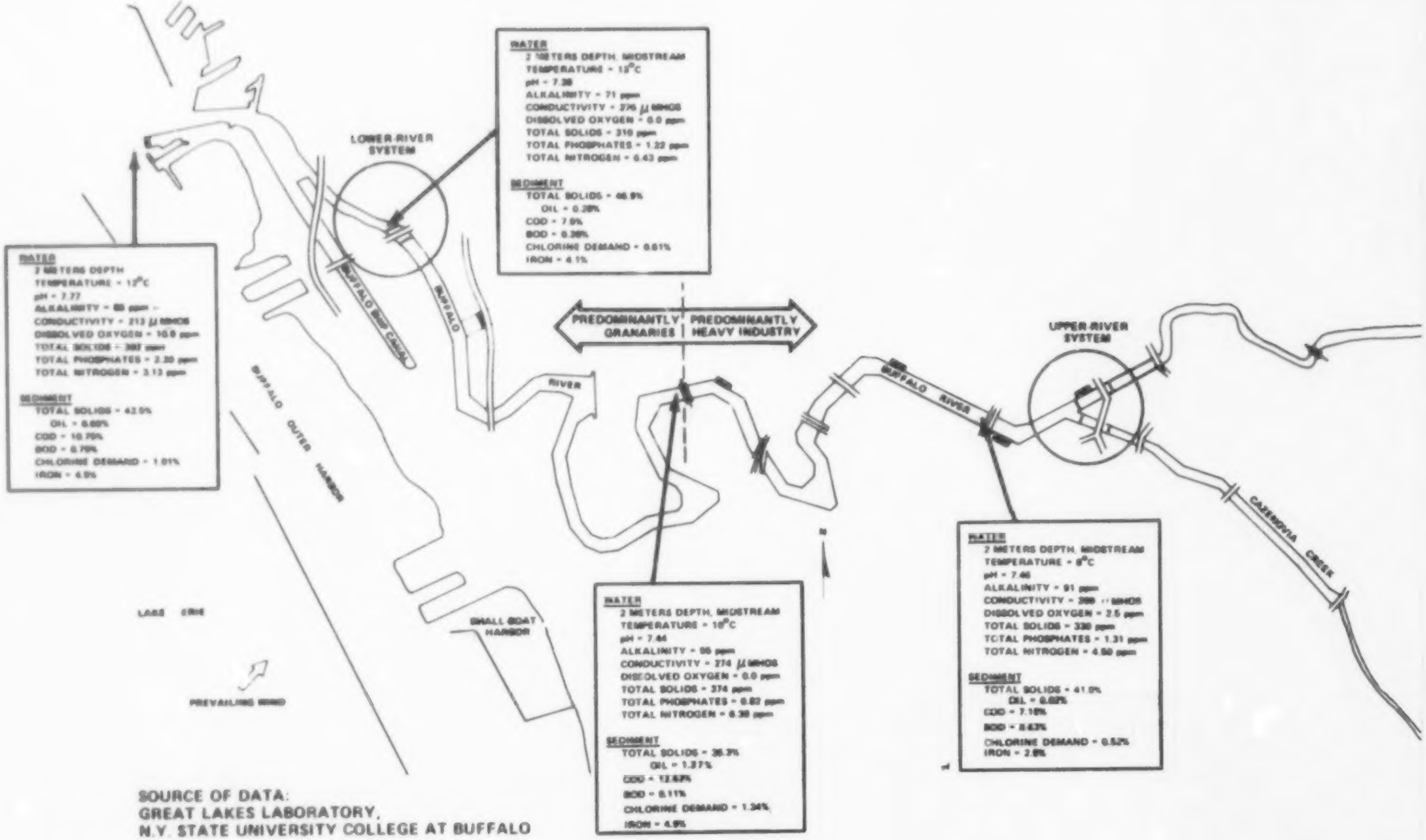
Figure 30 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 27 APRIL 1970


OIL
SURFACE = 2.1 ppm (SCREEN) & pH = 7.2
3 METERS DEPTH = 2.0 ppm & pH = 7.0
6 METERS DEPTH = 2.1 ppm & pH = 7.0
RIVER BOTTOM = 2.1 ppm
SEDIMENT = 0.08%
LOWER RIVER SYSTEM
OIL
SURFACE = 2.1 ppm
3 METERS DEPTH = 1.7 ppm
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO OUTER HARBOR
OIL
3 METERS DEPTH = 2.1 ppm
6 METERS DEPTH = 2.0 ppm
SEDIMENT = 0.01%
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
OIL
SURFACE = 1.0 ppm (SCREEN)
3 METERS DEPTH = 1.6 ppm
SEDIMENT = 0.09%
N
OIL
SURFACE = 2.0 ppm (SCREEN)
3 METERS DEPTH = 1.0 ppm
6 METERS DEPTH = 3.3 ppm
RIVER BOTTOM = 3.3 ppm
SEDIMENT = 1.01%
OIL
SURFACE = 2.9 ppm (SCREEN)
3 METERS DEPTH = 1.9 ppm & pH = 7.0
6 METERS DEPTH = 28.2 ppm & pH = 6.6
RIVER BOTTOM = 28.2 ppm
SEDIMENT = 0.87%
BUFFALO RIVER
UPPER RIVER SYSTEM
OIL
1 METER DEPTH = 1.2 ppm & pH = 7.1
6 INCH WATER TEMPERATURE = 53.6°F
OIL
SURFACE = 2.1 ppm (SCREEN)
1 METER DEPTH = 1.7 ppm
RIVER BOTTOM = 1.7 ppm
CAZENOVIA CREEK

WEATHER: MOSTLY SUNNY, DENSE FOG FORMED OVER LAKE AND ADVECTED INLAND OVER RIVER AREA ABOUT HALFWAY THROUGH SAMPLING.
WIND WSW AT 12 mph, TEMPERATURE = 70°F,
RELATIVE HUMIDITY = 66%, ATMOSPHERIC PRESSURE = 30.00 in (AND FALLING), LAKE TEMPERATURE = 48°F.
1 ◊ OCCURRED THE DAY BEFORE

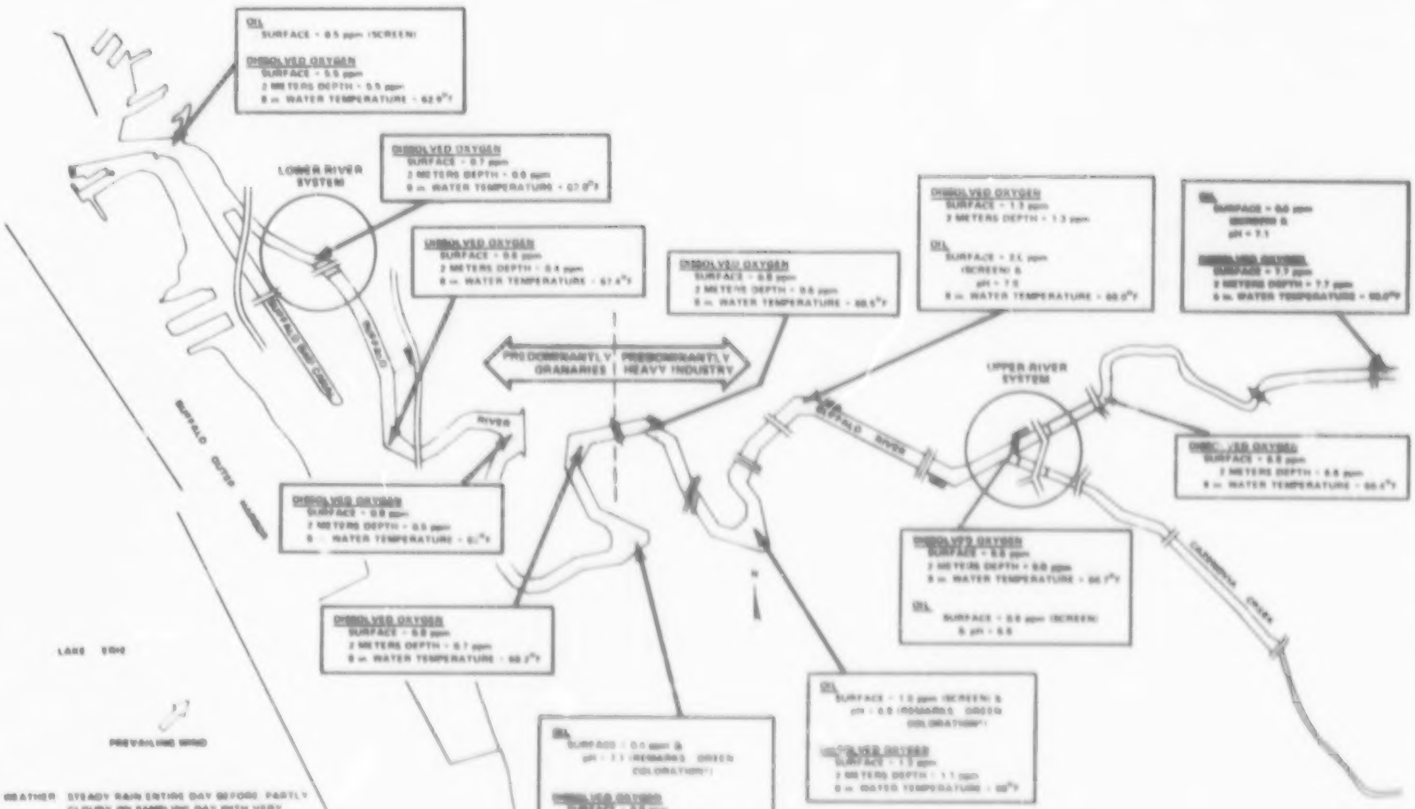
SOURCES OF DATA:
CORNELL AERONAUTICAL LABORATORY
AND BUFFALO SEWER AUTHORITY

Figure 31 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 11 MAY 1970


WATER
2 METERS DEPTH
TEMPERATURE = 12°C
pH = 7.77
ALKALINITY = 85 ppm
CONDUCTIVITY = 213 μ MHOS
DISSOLVED OXYGEN = 10.0 ppm
TOTAL SOLIDS = 302 ppm
TOTAL PHOSPHATES = 2.30 ppm
TOTAL NITROGEN = 3.13 ppm
SEDIMENT
TOTAL SOLIDS = 42.0%
OIL = 0.60%
COD = 10.70%
BOD = 0.79%
CHLORINE DEMAND = 1.01%
IRON = 4.9%
LOWER RIVER SYSTEM
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 12°C
pH = 7.38
ALKALINITY = 71 ppm
CONDUCTIVITY = 276 μ MHOS
DISSOLVED OXYGEN = 0.0 ppm
TOTAL SOLIDS = 310 ppm
TOTAL PHOSPHATES = 1.22 ppm
TOTAL NITROGEN = 6.43 ppm
SEDIMENT
TOTAL SOLIDS = 46.9%
OIL = 0.28%
COD = 7.9%
BOD = 0.28%
CHLORINE DEMAND = 0.61%
IRON = 4.1%
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO OUTER HARBOR
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO RIVER
UPPER RIVER SYSTEM
CAZENOVIA CREEK
N
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 10°C
pH = 7.44
ALKALINITY = 95 ppm
CONDUCTIVITY = 274 μ MHOS
DISSOLVED OXYGEN = 0.0 ppm
TOTAL SOLIDS = 374 ppm
TOTAL PHOSPHATES = 0.82 ppm
TOTAL NITROGEN = 6.38 ppm
SEDIMENT
TOTAL SOLIDS = 35.7%
OIL = 1.37%
COD = 12.62%
BOD = 0.11%
CHLORINE DEMAND = 1.34%
IRON = 4.9%
WATER
2 METERS DEPTH, MIDSTREAM
TEMPERATURE = 8°C
pH = 7.46
ALKALINITY = 91 ppm
CONDUCTIVITY = 289 μ MHOS
DISSOLVED OXYGEN = 2.5 ppm
TOTAL SOLIDS = 330 ppm
TOTAL PHOSPHATES = 1.31 ppm
TOTAL NITROGEN = 4.50 ppm
SEDIMENT
TOTAL SOLIDS = 41.0%
OIL = 0.02%
COD = 7.10%
BOD = 0.63%
CHLORINE DEMAND = 0.52%
IRON = 2.8%
LAKE ERIE
PREVAILING WIND
SMALL BOAT HARBOR

SOURCE OF DATA:
GREAT LAKES LABORATORY,
N.Y. STATE UNIVERSITY COLLEGE AT BUFFALO

Figure 32 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 13 MAY 1970


OIL
SURFACE = 0.5 ppm (SCREEN)
DISSOLVED OXYGEN
SURFACE = 5.5 ppm
2 METERS DEPTH = 5.5 ppm
0 m. WATER TEMPERATURE = 62.9°F
LOWER RIVER SYSTEM
DISSOLVED OXYGEN
SURFACE = 0.7 ppm
2 METERS DEPTH = 0.0 ppm
0 m. WATER TEMPERATURE = 67.0°F
DISSOLVED OXYGEN
SURFACE = 0.8 ppm
2 METERS DEPTH = 0.4 ppm
0 m. WATER TEMPERATURE = 67.4°F
DISSOLVED OXYGEN
SURFACE = 0.8 ppm
2 METERS DEPTH = 0.6 ppm
0 m. WATER TEMPERATURE = 68.5°F
DISSOLVED OXYGEN
SURFACE = 1.3 ppm
2 METERS DEPTH = 1.3 ppm
OIL
SURFACE = 2.C ppm
(SCREEN) &
pH = 7.0
0 m. WATER TEMPERATURE = 68.0°F
OIL
SURFACE = 0.0 ppm
(SCREEN) &
pH = 7.1
DISSOLVED OXYGEN
SURFACE = 7.7 ppm
2 METERS DEPTH = 7.7 ppm
0 m. WATER TEMPERATURE = 60.0°F
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
UPPER RIVER SYSTEM
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO RIVER
CAZENOVIA CREEK
BUFFALO OUTER HARBOR
DISSOLVED OXYGEN
SURFACE = 6.8 ppm
2 METERS DEPTH = 6.6 ppm
0 m. WATER TEMPERATURE = 60.4°F
DISSOLVED OXYGEN
SURFACE = 0.8 ppm
2 METERS DEPTH = 0.5 ppm
0 m. WATER TEMPERATURE = 6_°F
DISSOLVED OXYGEN
SURFACE = 6.6 ppm
2 METERS DEPTH = 6.6 ppm
0 m. WATER TEMPERATURE = 60.7°F
OIL
SURFACE = 0.0 ppm (SCREEN)
& pH = 6.6
N
DISSOLVED OXYGEN
SURFACE = 0.8 ppm
2 METERS DEPTH = 0.7 ppm
0 m. WATER TEMPERATURE = 68.2°F
OIL
SURFACE = 0.4 ppm &
pH = 7.1 (REMARKS: GREEN COLORATION*)
DISSOLVED OXYGEN
SURFACE = 5.8 ppm
2 METERS DEPTH = 0.5 ppm
0 m. WATER TEMPERATURE = 68.7°F
OIL
SURFACE = 1.0 ppm (SCREEN) &
pH = 6.0 (REMARKS: GREEN COLORATION*)
DISSOLVED OXYGEN
SURFACE = 1.3 ppm
2 METERS DEPTH = 1.1 ppm
0 m. WATER TEMPERATURE = 66°F
LAKE ERIE
PREVAILING WIND

WEATHER STEADY RAIN ENTIRE DAY BEFORE. PARTLY CLOUDY ON SAMPLING DAY WITH VERY LITTLE SHOWER AT ABOUT NOON. WINDS SW AT ABOUT 10 mph.

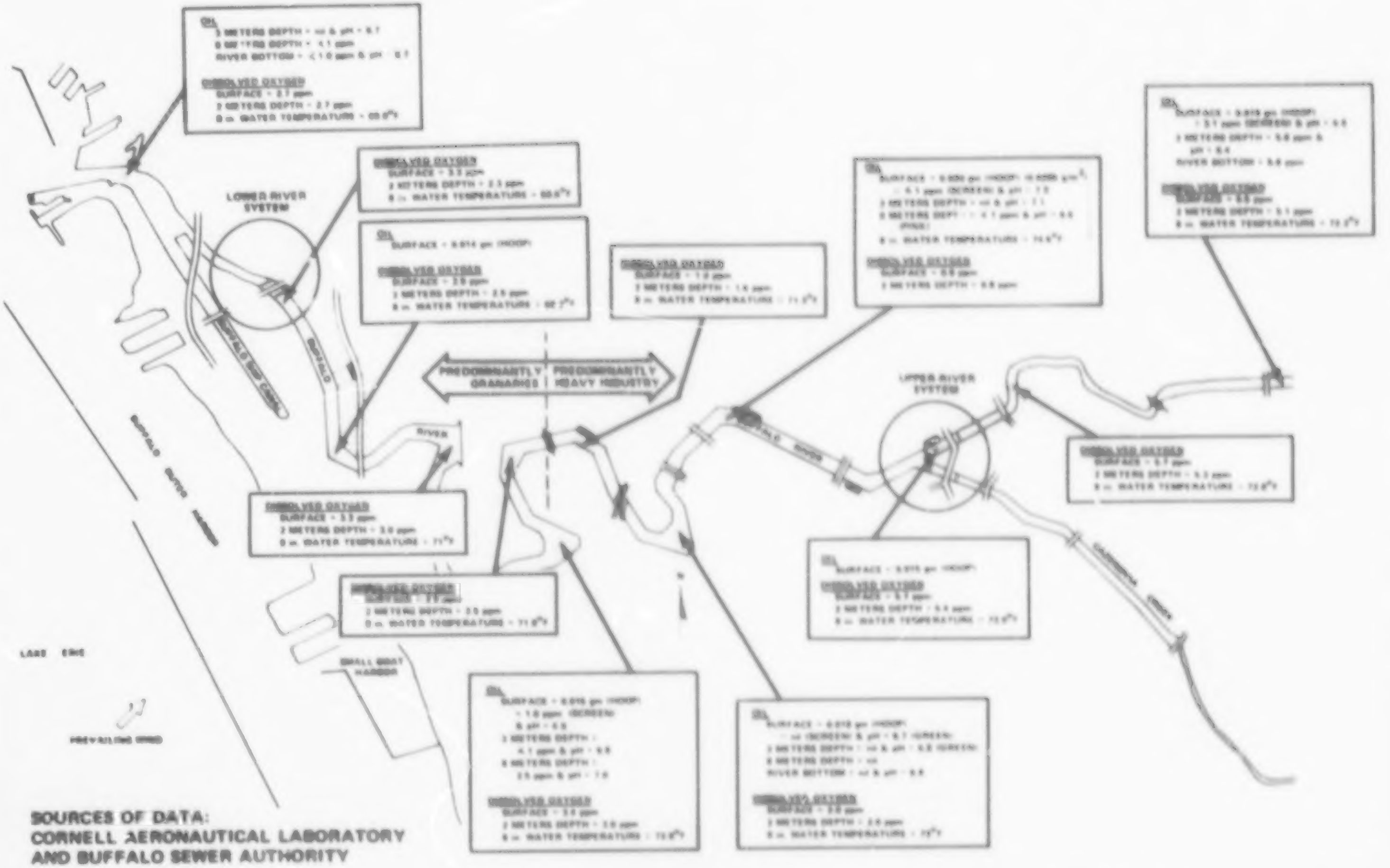
EVEN AFTER ALL THE RAIN, RIVER WAS RELATIVELY [illegible] FREE IN RESPECT TO SURFACE OIL. IT WAS THE DIRTIEST TO DATE EVEN UPSTREAM TO SAMPLING SITE 1

---

*GREEN COLORATION WAS IN THE CHLOROFORM EXTRACT

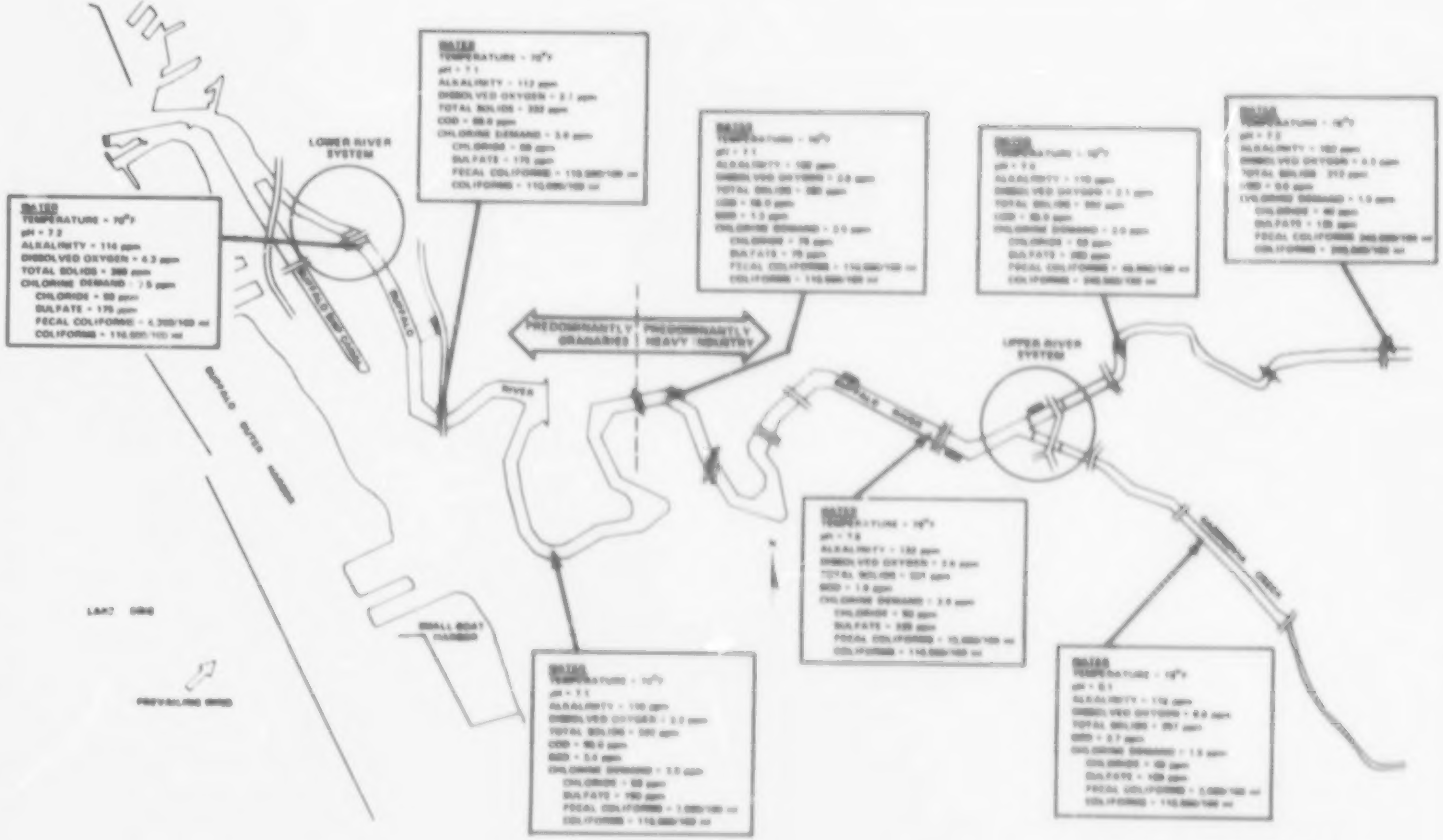
SOURCES OF DATA:
CORNELL AERONAUTICAL LABORATORY
AND BUFFALO SEWER AUTHORITY

Figure 33 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 25 MAY 1970


LOWER RIVER SYSTEM
UPPER RIVER SYSTEM
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO RIVER
BUFFALO SHIP CANAL
BUFFALO OUTER HARBOR
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND
CAZENOVIA CREEK
DISSOLVED OXYGEN

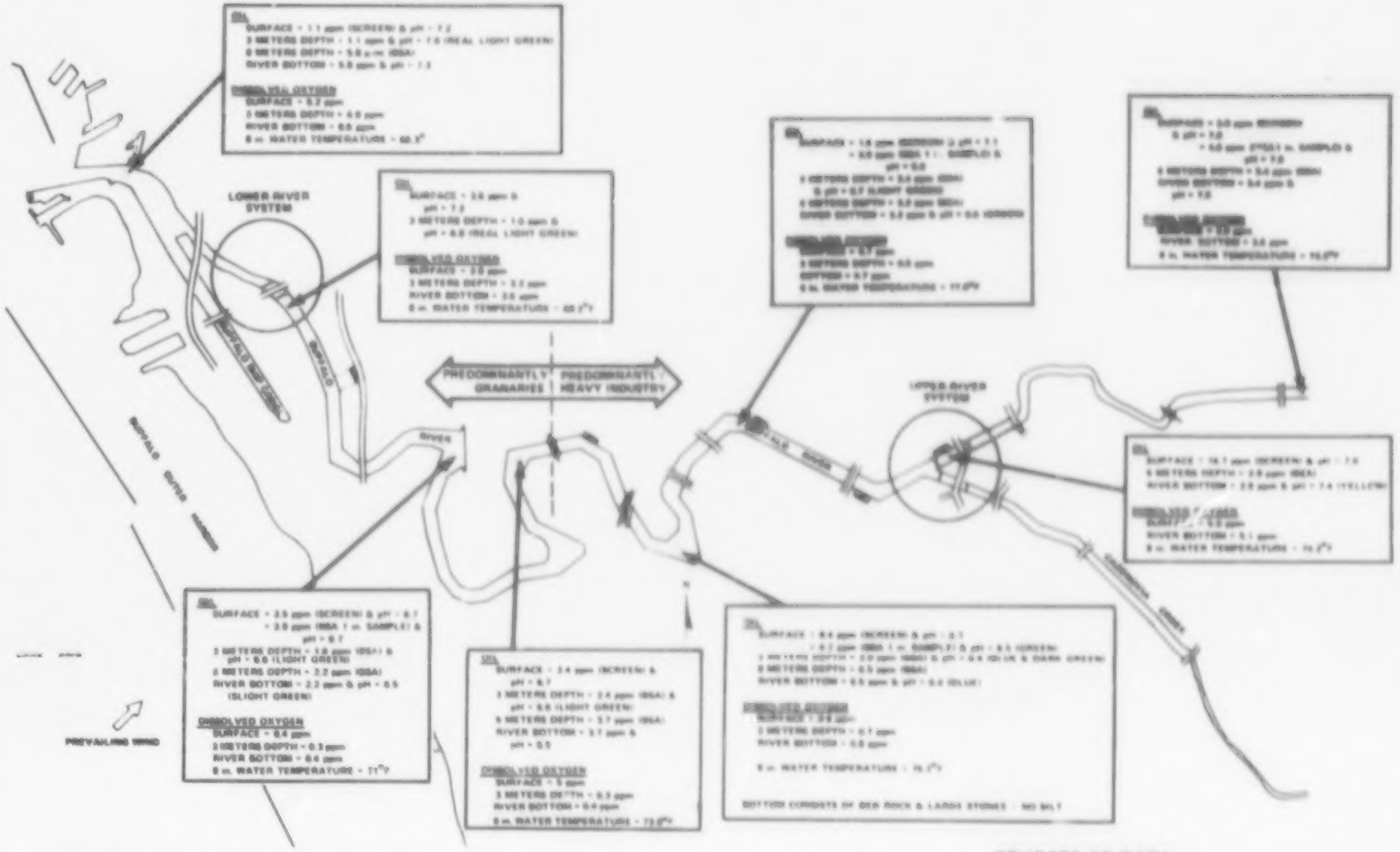
SOURCES OF DATA:
CORNELL AERONAUTICAL LABORATORY
AND BUFFALO SEWER AUTHORITY

Figure 34 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 1 JUNE 1970


LOWER RIVER SYSTEM
UPPER RIVER SYSTEM
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO
RIVER
BUFFALO SHIP CANAL
BUFFALO OUTER HARBOR
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND

SOURCE OF DATA:
BUFFALO SEWER AUTHORITY

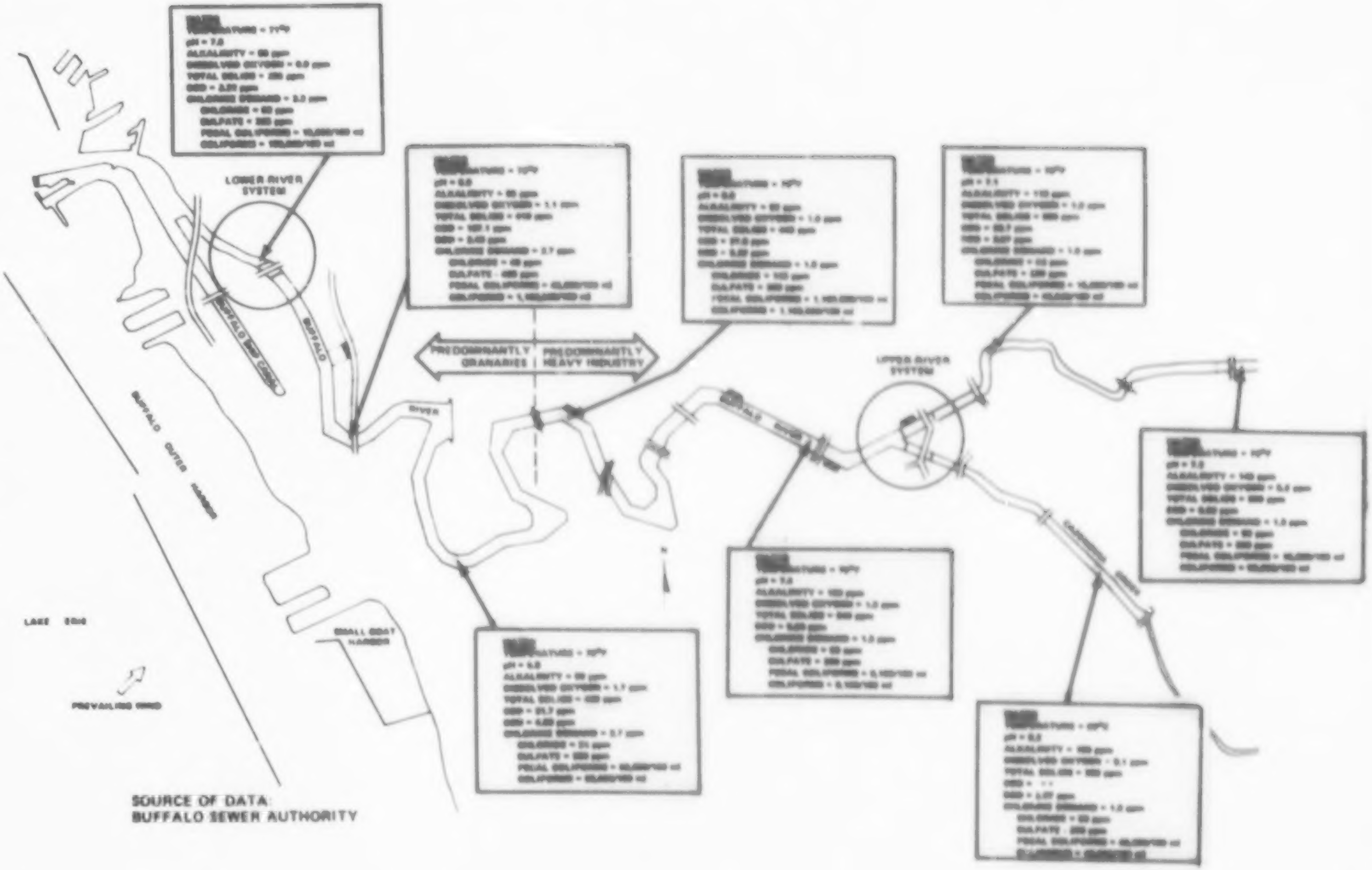
Figure 35 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 2 JUNE 1970


OIL
SURFACE = 1.1 ppm (SCREEN) & pH = 7.2
3 METERS DEPTH = 1.1 ppm & pH = 7.6 (REAL LIGHT GREEN)
6 METERS DEPTH = 5.0 ppm (DSA)
RIVER BOTTOM = 5.0 ppm & pH = 7.3
DISSOLVED OXYGEN
SURFACE = 5.2 ppm
3 METERS DEPTH = 4.0 ppm
RIVER BOTTOM = 0.0 ppm
8 m. WATER TEMPERATURE = 60.3°
LOWER RIVER SYSTEM
OIL
SURFACE = 2.0 ppm &
pH = 7.2
3 METERS DEPTH = 1.0 ppm &
pH = 6.8 (REAL LIGHT GREEN)
DISSOLVED OXYGEN
SURFACE = 2.0 ppm
3 METERS DEPTH = 2.2 ppm
RIVER BOTTOM = 2.0 ppm
8 m. WATER TEMPERATURE = 68.2°F
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO SHIP CANAL
BUFFALO RIVER
BUFFALO OUTER HARBOR
UPPER RIVER SYSTEM
CAZENOVIA CREEK
PREVAILING WIND
OIL
SURFACE = 2.5 ppm (SCREEN) & pH = 6.1
= 3.0 ppm (DSA 1 m. SAMPLE) &
pH = 6.7
3 METERS DEPTH = 1.8 ppm (DSA) &
pH = 6.8 (LIGHT GREEN)
6 METERS DEPTH = 2.2 ppm (DSA)
RIVER BOTTOM = 2.2 ppm & pH = 6.5
(SLIGHT GREEN)
DISSOLVED OXYGEN
SURFACE = 0.4 ppm
3 METERS DEPTH = 0.3 ppm
RIVER BOTTOM = 0.4 ppm
8 m. WATER TEMPERATURE = 71°F
OIL
SURFACE = 2.4 ppm (SCREEN) &
pH = 6.7
3 METERS DEPTH = 2.4 ppm (DSA) &
pH = 6.6 (LIGHT GREEN)
5 METERS DEPTH = 3.7 ppm (DSA)
RIVER BOTTOM = 3.7 ppm &
pH = 6.5
DISSOLVED OXYGEN
SURFACE = 5 ppm
3 METERS DEPTH = 0.3 ppm
RIVER BOTTOM = 0.4 ppm
8 m. WATER TEMPERATURE = 73.0°F
DISSOLVED OXYGEN
8 m. WATER TEMPERATURE
BOTTOM CONSISTS OF BED ROCK & LARGE STONES – NO SILT

4 SAMPLES FROM NATIONAL ANILINE (1 FOAM, 1 PURPLE, 1 BLUE, 1 OILY OUTFALL MIXED WITH RIVER WATER)
1 FROM MOBIL OIL CO
1 FROM REPUBLIC STEEL CO. AND
1 FROM AMERICAN MALT CO

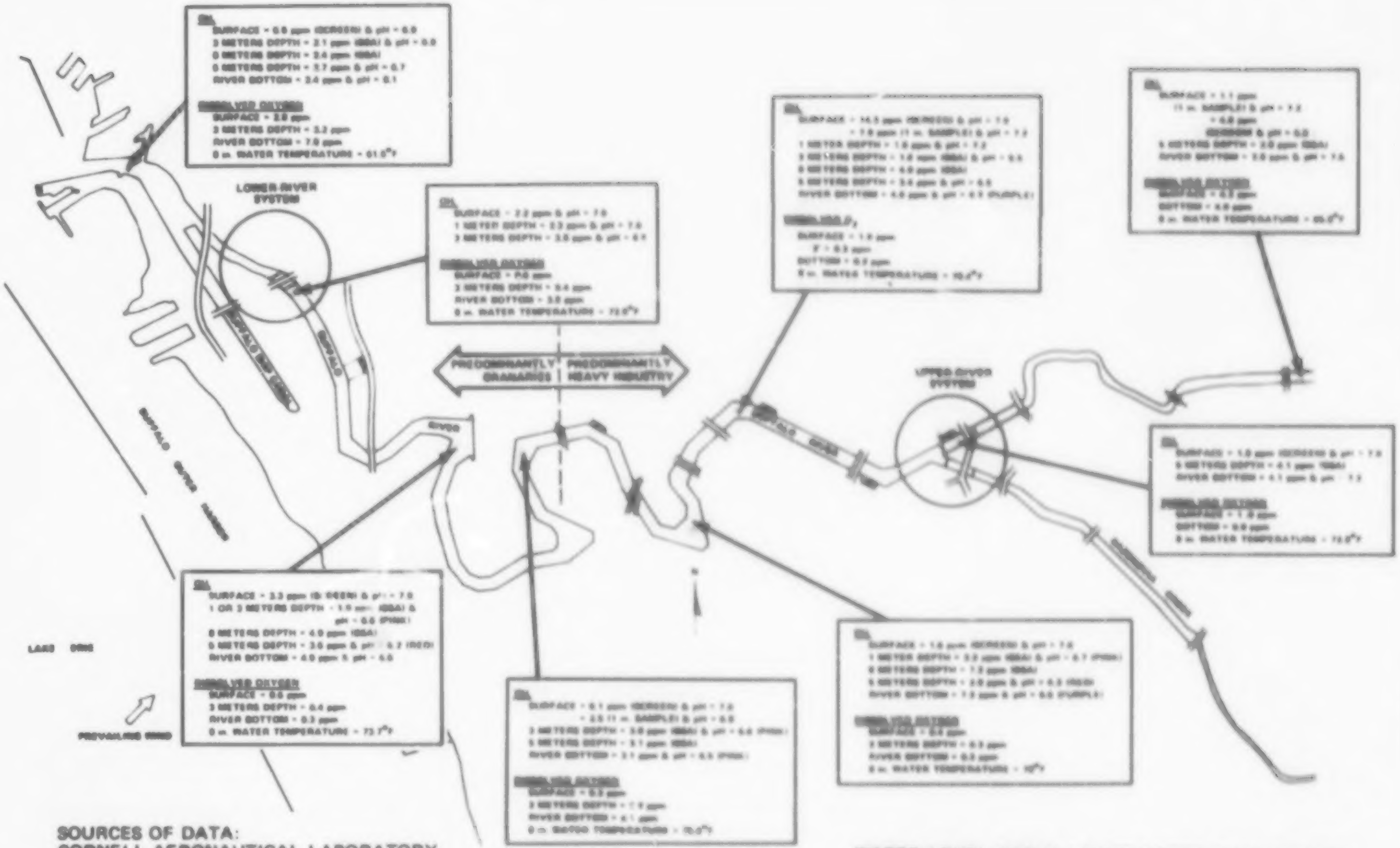
SOURCES OF DATA:
CORNELL AERONAUTICAL LABORATORY
AND BUFFALO SEWER AUTHORITY

Figure 36 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 15 JUNE 1970


LOWER RIVER SYSTEM
UPPER RIVER SYSTEM
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO
RIVER
BUFFALO SHIP CANAL
BUFFALO OUTER HARBOR
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND

SOURCE OF DATA:
BUFFALO SEWER AUTHORITY

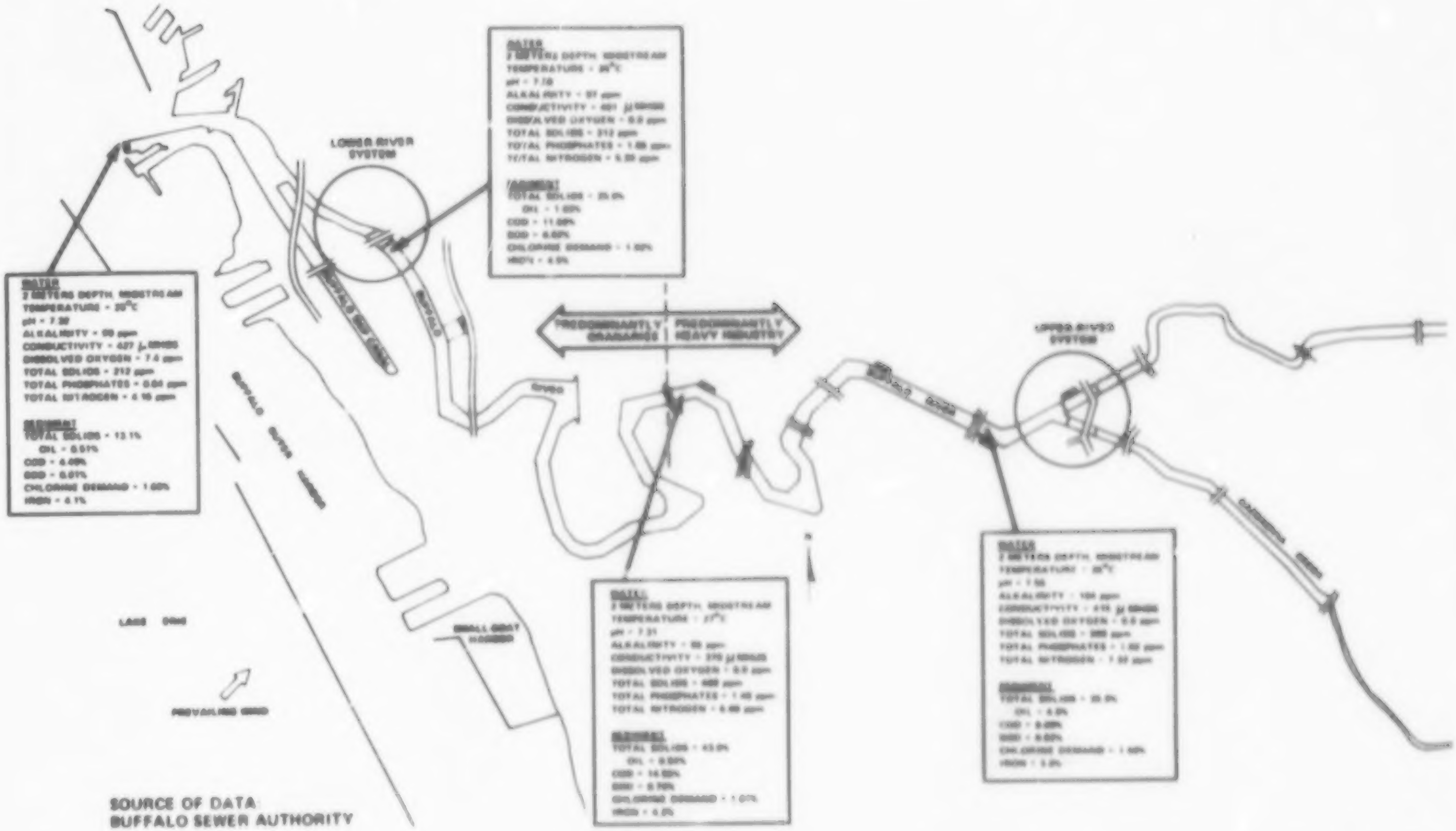
Figure 37 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 16 JUNE 1970


LOWER RIVER SYSTEM
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
UPPER RIVER SYSTEM
BUFFALO OUTER HARBOR
BUFFALO RIVER
LAKE ERIE
PREVAILING WIND
DISSOLVED OXYGEN
SURFACE
RIVER BOTTOM
WATER TEMPERATURE

SOURCES OF DATA:
CORNELL AERONAUTICAL LABORATORY
AND BUFFALO SEWER AUTHORITY

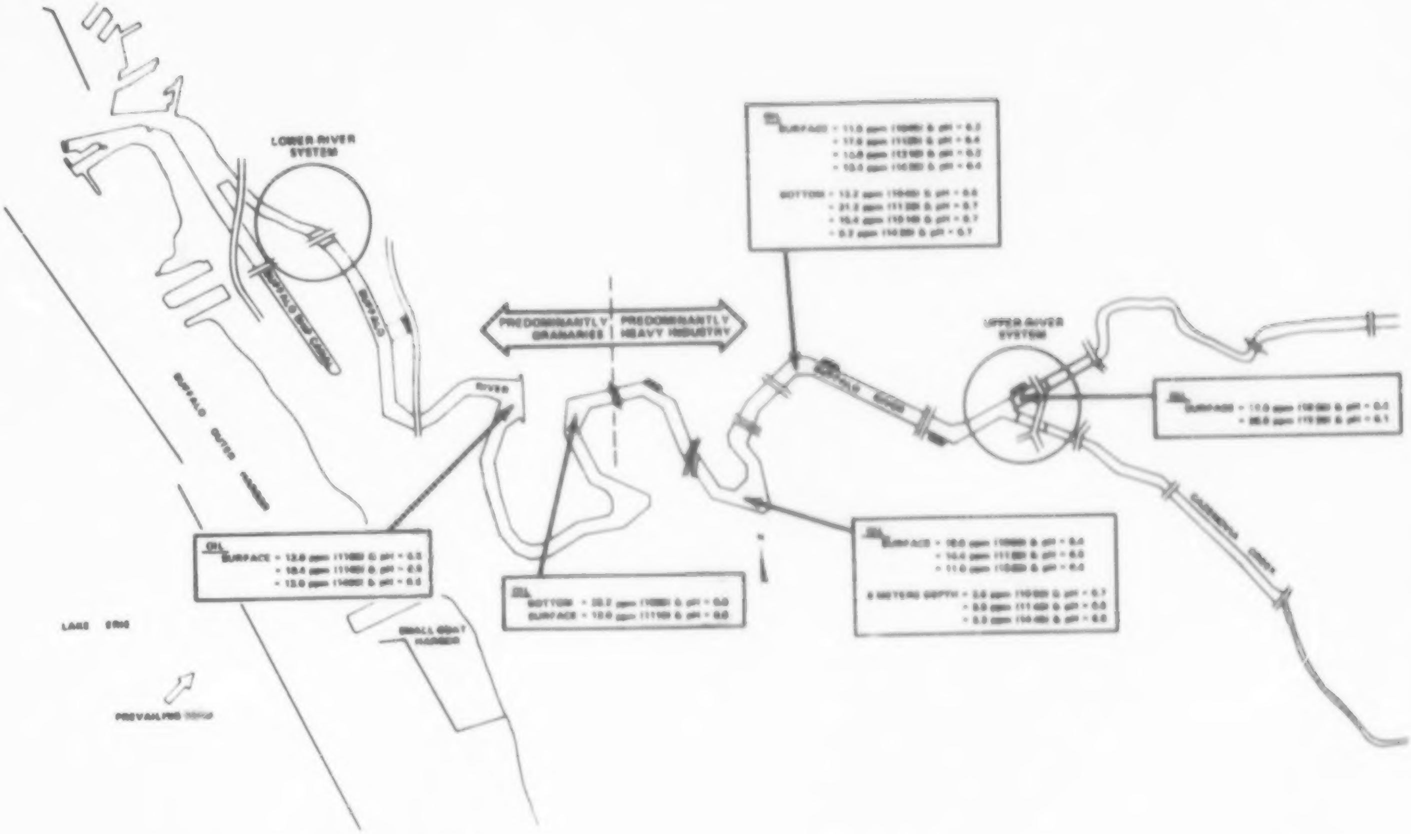
WATER LEVEL ABOUT 1 FOOT LOWER THAN DURING PREVIOUS WEEKS; SOME LARGE DEAD CARP SEEN IN UPPER STRETCHES.

Figure 38 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 22 JUNE 1970


WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 20°C
pH = 7.30
ALKALINITY = 99 ppm
CONDUCTIVITY = 427 µ MHOS
DISSOLVED OXYGEN = 7.4 ppm
TOTAL SOLIDS = 212 ppm
TOTAL PHOSPHATES = 0.04 ppm
TOTAL NITROGEN = 4.16 ppm
SEDIMENT
TOTAL SOLIDS = 13.1%
OIL = 0.51%
COD = 4.09%
BOD = 0.01%
CHLORINE DEMAND = 1.60%
IRON = 4.1%
LOWER RIVER SYSTEM
WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 20°C
pH = 7.10
ALKALINITY = 97 ppm
CONDUCTIVITY = 401 µ MHOS
DISSOLVED OXYGEN = 6.0 ppm
TOTAL SOLIDS = 312 ppm
TOTAL PHOSPHATES = 1.06 ppm
TOTAL NITROGEN = 5.20 ppm
SEDIMENT
TOTAL SOLIDS = 20.0%
OIL = 1.00%
COD = 11.00%
BOD = 6.00%
CHLORINE DEMAND = 1.00%
IRON = 4.0%
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO SHIP CANAL
BUFFALO RIVER
BUFFALO OUTER HARBOR
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND
WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 27°C
pH = 7.21
ALKALINITY = 90 ppm
CONDUCTIVITY = 270 µ MHOS
DISSOLVED OXYGEN = 0.0 ppm
TOTAL SOLIDS = 400 ppm
TOTAL PHOSPHATES = 1.40 ppm
TOTAL NITROGEN = 6.00 ppm
SEDIMENT
TOTAL SOLIDS = 43.0%
OIL = 0.50%
COD = 14.50%
BOD = 0.70%
CHLORINE DEMAND = 1.07%
IRON = 4.0%
BUFFALO RIVER
UPPER RIVER SYSTEM
WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 20°C
pH = 7.56
ALKALINITY = 100 ppm
CONDUCTIVITY = 410 µ MHOS
DISSOLVED OXYGEN = 6.6 ppm
TOTAL SOLIDS = 300 ppm
TOTAL PHOSPHATES = 1.00 ppm
TOTAL NITROGEN = 7.30 ppm
SEDIMENT
TOTAL SOLIDS = 20.0%
OIL = 4.0%
COD = 8.00%
BOD = 0.60%
CHLORINE DEMAND = 1.40%
IRON = 3.0%
CAZENOVIA CREEK

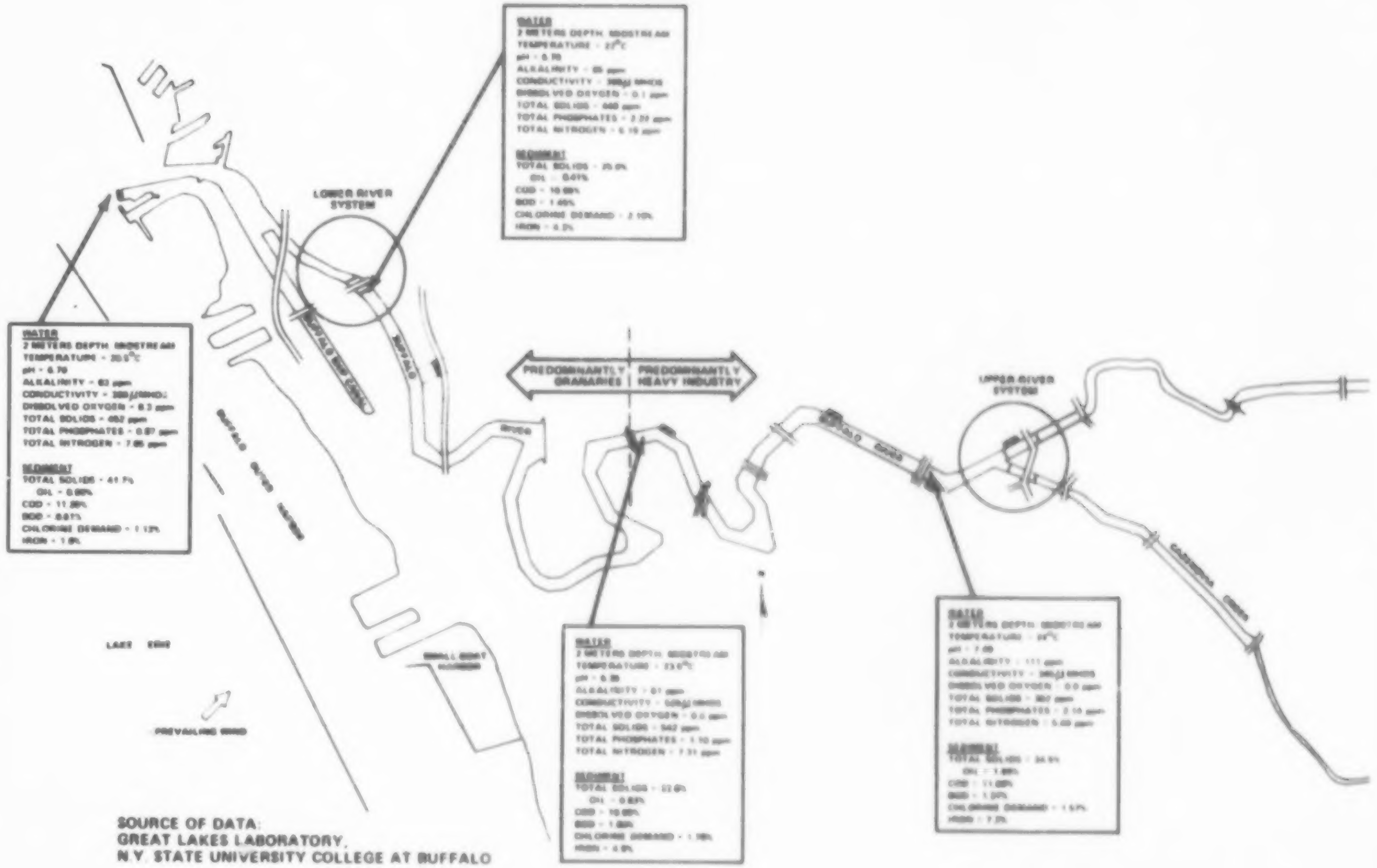
SOURCE OF DATA:
BUFFALO SEWER AUTHORITY

Figure 39 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 13 AUGUST 1970


LOWER RIVER SYSTEM
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO OUTER HARBOR
LAKE ERIE
PREVAILING WIND
SMALL BOAT HARBOR
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
OIL
SURFACE
BOTTOM
BUFFALO RIVER
UPPER RIVER SYSTEM
CAZENOVIA CREEK

SOURCES OF DATA:
CORNELL AERONAUTICAL LABORATORY
AND BUFFALO SEWER AUTHORITY

Figure 40 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 30 SEPTEMBER 1970


LOWER RIVER SYSTEM
UPPER RIVER SYSTEM
PREDOMINANTLY GRANARIES
PREDOMINANTLY HEAVY INDUSTRY
BUFFALO SHIP CANAL
BUFFALO
RIVER
BUFFALO CREEK
CAZENOVIA CREEK
BUFFALO OUTER HARBOR
SMALL BOAT HARBOR
LAKE ERIE
PREVAILING WIND
WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 20.5°C
pH = 6.70
ALKALINITY = 62 ppm
CONDUCTIVITY = 380 μMHOS
DISSOLVED OXYGEN = 8.3 ppm
TOTAL SOLIDS = 452 ppm
TOTAL PHOSPHATES = 0.57 ppm
TOTAL NITROGEN = 7.85 ppm
SEDIMENT
TOTAL SOLIDS = 41.7%
OIL = 0.90%
COD = 11.38%
BOD = 0.81%
CHLORINE DEMAND = 1.12%
IRON = 1.8%
WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 22°C
pH = 6.70
ALKALINITY = 85 ppm
CONDUCTIVITY = 390 μMHOS
DISSOLVED OXYGEN = 0.1 ppm
TOTAL SOLIDS = 440 ppm
TOTAL PHOSPHATES = 2.20 ppm
TOTAL NITROGEN = 6.19 ppm
SEDIMENT
TOTAL SOLIDS = 25.0%
OIL = 0.41%
COD = 10.88%
BOD = 1.46%
CHLORINE DEMAND = 2.10%
IRON = 4.2%
WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 23.0°C
pH = 6.35
ALKALINITY = 81 ppm
CONDUCTIVITY = 520 μMHOS
DISSOLVED OXYGEN = 0.0 ppm
TOTAL SOLIDS = 542 ppm
TOTAL PHOSPHATES = 1.10 ppm
TOTAL NITROGEN = 7.31 ppm
SEDIMENT
TOTAL SOLIDS = 22.0%
OIL = 0.83%
COD = 10.88%
BOD = 1.80%
CHLORINE DEMAND = 1.78%
IRON = 4.9%
WATER
2 METERS DEPTH MIDSTREAM
TEMPERATURE = 24°C
pH = 7.00
ALKALINITY = 111 ppm
CONDUCTIVITY = 380 μMHOS
DISSOLVED OXYGEN = 0.0 ppm
TOTAL SOLIDS = 357 ppm
TOTAL PHOSPHATES = 2.16 ppm
TOTAL NITROGEN = 5.03 ppm
SEDIMENT
TOTAL SOLIDS = 34.5%
OIL = 1.88%
COD = 11.08%
BOD = 1.37%
CHLORINE DEMAND = 1.57%
IRON = 7.2%

SOURCE OF DATA:
GREAT LAKES LABORATORY,
N.Y. STATE UNIVERSITY COLLEGE AT BUFFALO

Figure 41 WATER AND SEDIMENT QUALITY PROFILE OF BUFFALO RIVER FOR 27 OCTOBER 1970

The major finding, which may be validated by even casual inspection of Figures 24 through 41, is that there were always gross changes manifested in the River in its industrial sector (in Figure 2, the stretch between sampling sites 3/4--the confluence of the Buffalo River with two feeder tributaries upstream of the industrial section--and sampling Site 7--immediately downstream from the heavy concentration of industry) The data available from the 1964 sampling season show that the inflow waters to this industrial section had a relatively high pH (approximately 8) and that the waters during their transit through this industrial section dropped markedly (3 complete pH units) to approximately pH 5. The most grossly polluted site in the Buffalo River even today, labelled the South Park Avenue Lift Bridge site (E in Figure 2), is in the midst of this industrial sector. In addition to the pH changes over the course of this short distance, the conductivity of the waters doubled or tripled, the total solids carried in the bulk volume doubled or tripled,and the dissolved oxygen dropped from a near-saturated value to a near-zero value. All of these parameters reversed their trends once past Site 7 and on occasion recovered almost completely their upstream values (that is, the values typical of the river discharge waters before admixing with industrial effluents) before reaching the mouth at Lake Erie.

The information accumulated in Figures 26 through 41 for the 1968, 1969 and 1970 seasons postdates the introduction of the Buffalo River Improvement Project. Under this Project at least 100,000,000 gallons of water per day are pumped from Lake Erie into the industrial section of the River by industries which use the water for cooling purposes. The objective of diverting Lake Erie water into the River is to augment stream flow and dilute pollutant loads. It will be noted from inspection of the figures and other data presented in this report that the upstream inflow water during this time also became less alkaline as a result of control measures instituted by municipalities upstream. Therefore, between 1964 and 1970, the water entering the industrial segment of the River was less basic and, with the flow augmentation due to the cooling water project, it was also less acidic upon entering the downstream portions of the Buffalo River. Still, a pH change of about 1/2 to 1 unit, reflecting the addition of large amounts of acidic pollutants, was noted during the 1969 and 1970 seasons. The conductivity and total solids still showed marked increases during the transit of water through this segment and, even after the introduction of the minimum flow of 100,000,000 gallons per day, the dissolved oxygen still dropped to nearly zero in the industrial segment. Again, a slow recovery in the downstream waters was noted. The bottom sediment improved markedly in its freedom from oils and iron during the 1968-1970 period, however.

The results of oil content analysis for the sampling days during the 1969 season are not included on the charts given as Figures 28 and 29 because of the previously mentioned uncertainties of the hexane extraction technique. However typical results for three sampling days are shown in Table 6. These values were obtained by the hexane extraction method as performed by the Buffalo Sewer Authority Chemistry Laboratory. Even though it was found, after advanced analysis described in previous sections, that certain of the hydrocarbons and fatty matter present were insoluble in hexane and also that the hexane extract values were falsely inflated by probable trapping of extraction solvents in the final weight samples, the general trend of the oil content is very clear. The oil content peaked, often dramatically, in the industrial segment. (As a rough correction factor, it has been suggested earlier that the values expressed in Table 6 for oil concentration be reduced by a factor of 2 to provide values more comparable with the values later obtained by the chloroform extraction technique.)

Table 6

TYPICAL BULK WATER DATA FOR 1969 SAMPLING PROGRAM

(HEXANE-EXTRACTABLE MATTER IN PPM)

SAMPLING DATE (1969)	APPROXIMATE LOCATION (SAMPLING SITE NO.)							
	2	3	5	6	7	9-10	10	11-12
20 AUGUST	4.4	4.4	11.8	7.7	5.1	10.8	1.7	1.2
11 SEPTEMBER	1.6	6.4	3.2	7.8	1.0	0.6	5.9	5.1
4 NOVEMBER	–	3.7	55.6	6.5	11.1	14.2	23.7	7.0

During 1968, 1969 and 1970 there was also an increase, indeed a doubling in some cases, in the chemical oxygen demand (COD) of the Buffalo River water during its transit through the very short industrialized section, and concomitantly an apparent decrease in the biochemical oxygen demand (BOD). Thus, we noted simultaneously a large increase in oil, a large increase in acidity and in dissolved solids, and a misleading decrease in BOD. This BOD decrease was also correlated, as can be seen from scanning the summary charts, with a large decrease in culturable coliform bacteria on the River's transit through the industrial section. Thus, the industrial effluents have a large killing effect on sewage-spawned bacteria known to be added to the Buffalo River upstream. This mention of the biological qualities of the River should be augmented briefly by reference to the bulk water quality in terms of its organic pollutants of biological origin. Such pollutants were not the subject of inquiry in this program but, nonetheless, should be considered in any comprehensive industrial watercourse study.

For example, most Buffalo River water samples, even those having a strikingly different character in terms of their dissolved substances (for example, even differing grossly in color from green to red to brown) showed definitive evidence for the presence of plentiful biological materials solubilized in the River water. Figure 42 shows a

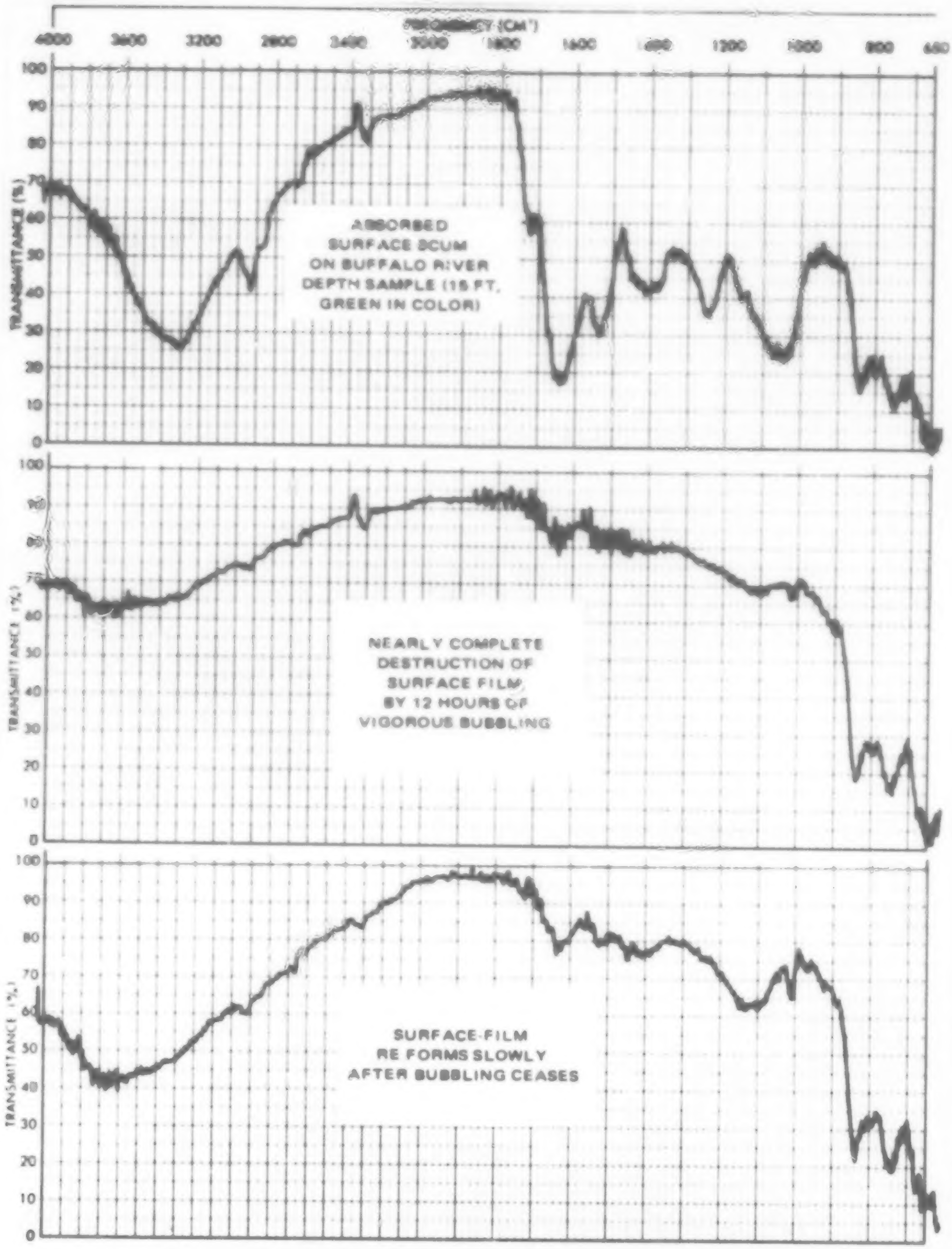


Figure 42 INFRARED EVIDENCE FOR THE PRESENCE OF SIGNIFICANT QUANTITIES OF DISSOLVED BIOLOGICAL SUBSTANCES IN BUFFALO RIVER WATER

sequence of spectra characterizing surface films which adsorb spontaneously from such bulk river water samples. The top spectrum in Figure 42 represents the appreciable scum which accumulated on Buffalo River water samples taken slightly down river from the highly industrialized section. This spectrum represents substances almost exclusively of biological origin: fats, proteins, and polysaccharrides. Such quantities of biological substances in the River are not surprising. It will be noted from inspection of Figure 2 that there are numerous sewer overflows along the River, and it was further observed by our sampling crew that copious effluents enter the River, even in its industrialized section, from overflow pipes from food processing plants and from the granaries. The potential difficulty with suspended and dissolved organic materials in the River, including those of biological origin, is that the degradative biological activity (due to the natural bacteria there) is severely depressed in the industrial segments of the River, which have almost zero dissolved oxygen.

Comparing changes in water chemistry between the sampling sites on any given date, the highest values of pollutants and the overall poorest water quality was always measured in the midst of the industrialized section (Sampling Sites 5 and 6, in Figure 2) and, in particular near the South Park Avenue Lift Bridge Site (E in Figure 2). For example, in this region during most of each summer season, the dissolved oxygen at all times and at all depths was measured as 0.0, while the ammonia concentration was 4.4 ppm or higher (data from the Great Lakes Laboratory). Ammonia concentrations above 2 ppm are considered to be toxic to most desirable forms of life in waterways. Better water quality was always observed near the mouth of the River where some mixing with the more-oxygenated lake water occurs. Reports by the Great Lakes Laboratory showed that the 1969 and 1970 seasons had a marked decline in conductivity and of dissolved solids in the River while the suspended solids increased. The ammonia and total nitrogen levels were generally higher in the latter year as well. The quality of the sediment, as will be discussed later, generally improved particularly in respect to its oil content, its chemical and biochemical oxygen demand and its chlorine demand. Iron continued to remain high in the bottom sediment in the industrialized section.

Because of the previously mentioned freezing-over of the upper reaches of the Buffalo River, and the presence of skim and chunk ice over the complete River surface during the winter season, the sampling and analysis efforts were sharply curtailed during these periods. However, a sampling series in late 1969 and early 1970 was carried out on ice-covered portions of the Buffalo River, and these data should be presented briefly here to complete the characterization. Figure 43 shows infrared spectra characterizing four different types of samples obtained during this winter season. Figure 43, Trace A, characterizes a sample taken with a ladle from the River surface zone immediately after the ice cover was removed. This spectrum shows a notable absence of oily materials but does provide evidence of suspended silica particles (soil) and also of considerable proteinaceous matter (note the strong

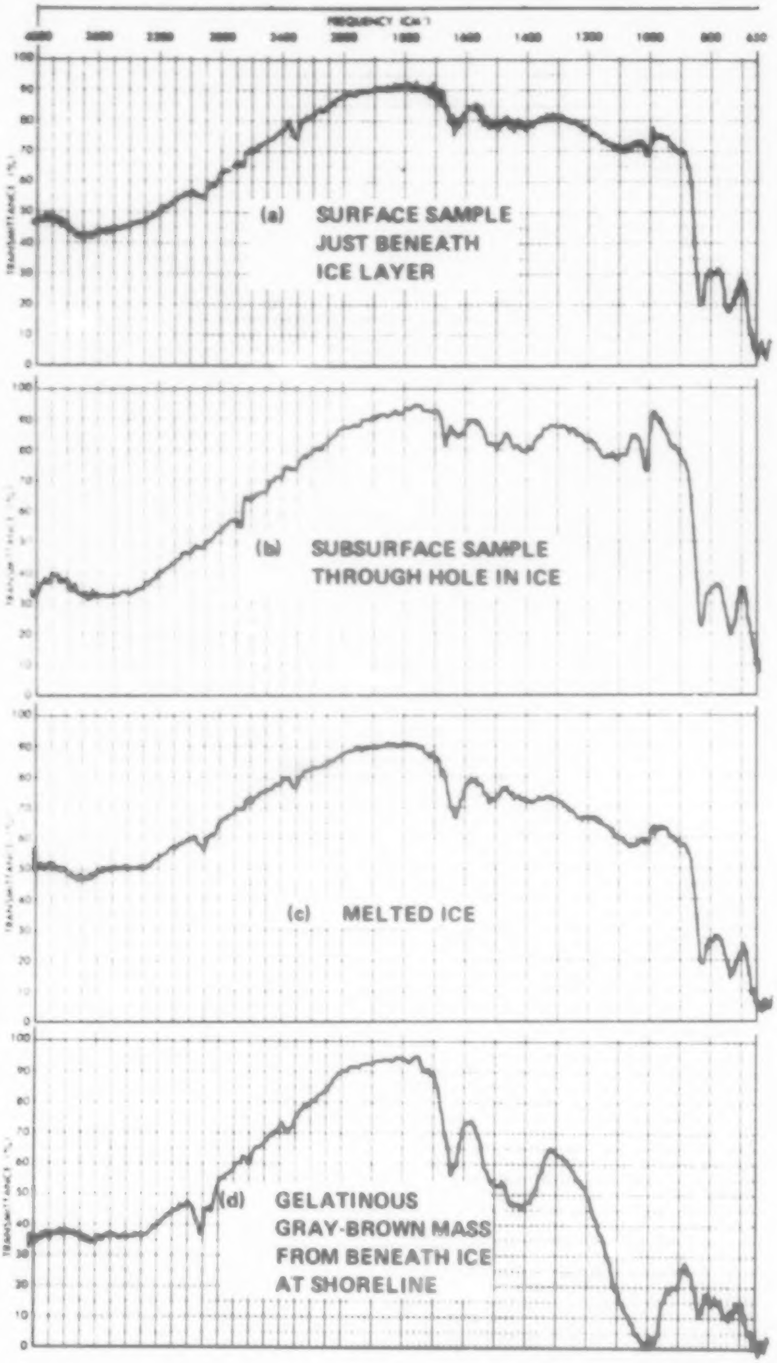


Figure 43 INFRARED SPECTRA OBTAINED BY PRISM DIP IN BUFFALO RIVER SAMPLES TAKEN IN JANUARY 1970

absorption band in the 1600 cm^{-1} region). Trace B in this figure is a similarly bland spectrum characterizing samples of the sub-surface water (about 1 meter depth) from the same site. Here, again, the absorption bands can be generally attributed to a variety of dissolved solids and suspended inorganic matter. Although evidence of the presence of significant quantities of oil is not apparent here, the methods used did not favor detection of emulsified or otherwise solubilized hydrocarbon pollutants because large quantities of the water were not obtained for solvent extraction. Rather, these spectra were produced by simple drying of aliquots of the water onto internal reflection prisms as described earlier.

Trace C in Figure 43 characterizes the surface-active organic matter released from melted Buffalo River ice. Small quantities of oil were present, but the major portion of the ice-occluded organic matter appeared to be biological in substance. Trace D in this same figure characterizes the viscous, semi-solid, and (with warming) septic mass found in abundance along the river shoreline just beneath the ice cover. The infrared spectrum shows absorption bands which can be correlated with significant amounts of oily matter, even greater amounts of biological matter, and in addition many trapped inorganic materials, largely carbonates and silicates. In all the cases illustrated, the origin of the relatively large quantities of proteinacious materials were most likely from sewage entering the River upstream of the sampling point and trapped by the frozen surface layers.

Throughout these efforts to completely characterize water quality in this major industrial waterway, there were certain factors which were not under our control. For example, dredging by the Army Corps of Engineers occurred throughout the River in late summer to early fall of each year. Another factor that was uncontrollable was the fluctuation in the lake level which could vary significantly over the course of a given season. The higher the lake, the lower the net discharge of the river. For example, the lake level was approximately 30 cm higher during the 1969 sampling period than it had been in 1968. Thus the average discharge in 1969 was less than in 1968.

PROFILES OF THE BULK WATER BURDEN OF OILY POLLUTANTS

In general, in addition to obtaining samples of the apparent oil slicks, bulk water samples were taken in the immediate sub-surface zone using bag sampling and the surface screen techniques described earlier. Bulk water samples were taken using a Kemmerer bottle at depths of one, three, four, five, and eight meters. Not all these depths were sampled at each of the twelve sampling points on each occasion.

Figure 2 in the introductory section shows the location of the major bridges, sewer overflows, and industries near the sampling sites selected for this program. Table 7 fixes the location of each of these sampling sites by noting the distance from the lighthouse located at the south end of a breakwater in the Buffalo River Harbor. Graphical presentations of the data in the following figures include the sampling point location as a function of displacement from the lighthouse. In 1970 alone, nearly 300 samples of bulk water were taken from the River and were analyzed either at Cornell Aeronautical Laboratory or the Buffalo Sewer Authority Chemistry Laboratory. These data are abstracted in the figures described next.

Table 7

STREAM MILEAGE DATA FOR VARIOUS SAMPLING SITES

SAMPLING SITE NO.	DISTANCE FROM LIGHTHOUSE (MILES)
1	8.5
2	6.9
3	6.25 (BFLO. CREEK)
4	6.25 (CAZ. CREEK)
5	5.4
6	4.75
7	4.25
8	3.8
9	3.5
10	2.5
11	2.1
12	0.5
PREDOMINANTLY GRANARIES	TO 4.1 MILES
PREDOMINANTLY HEAVY INDUSTRY	UPSTREAM OF 4.1 MILES

Figure 44 is a graphical profile of chloroform-extractable material found in the surface water when samples were taken by the screen dip technique. Profiles for seven individual sampling dates are presented together with an average profile for all the data on all dates. Figure 44 demonstrates the much higher surface burden of oils found in the vicinity of the heavy industries along the River as contrasted to both the upstream and downstream portions.

Figure 45 includes profiles of the Buffalo River at the three meter depth and illustrates a similar variance in concentration (but to a much lesser degree). Figure 46, on the other hand, shows the dramatic increase in oily pollutants in the bottom waters in the River in its mostly highly industrialized section. It is obvious from the profiles presented in these figures that the chloroform-extractable pollutant burden at the surface and at the bottom of the Buffalo River is being introduced and concentrated between points 4.1 and 6 miles upstream

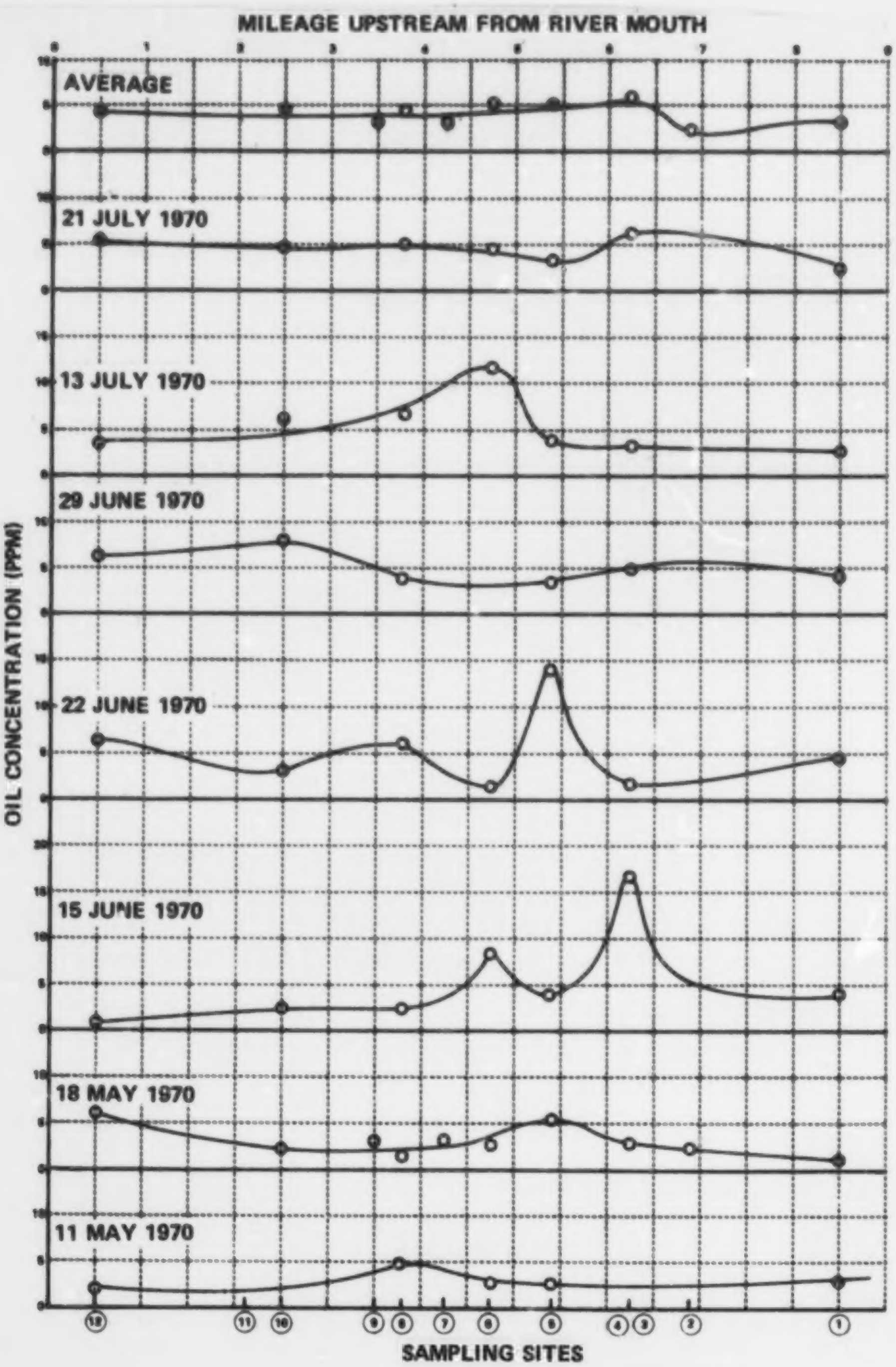


Figure 44 PROFILES OF BUFFALO RIVER SURFACE-WATER BURDEN OF CHLOROFORM-EXTRACTABLE OILY POLLUTANTS

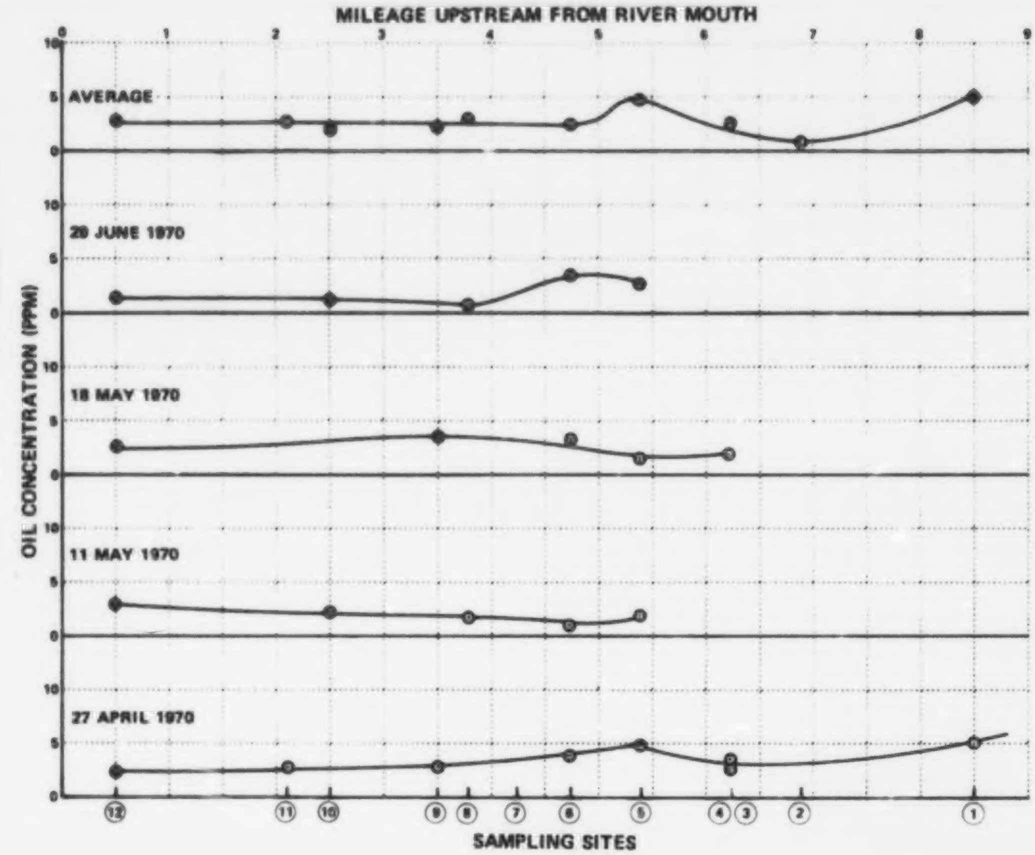


Figure 45 PROFILES OF BUFFALO RIVER BULK-WATER BURDEN OF CHLOROFORM-EXTRACTABLE OILY POLLUTANTS

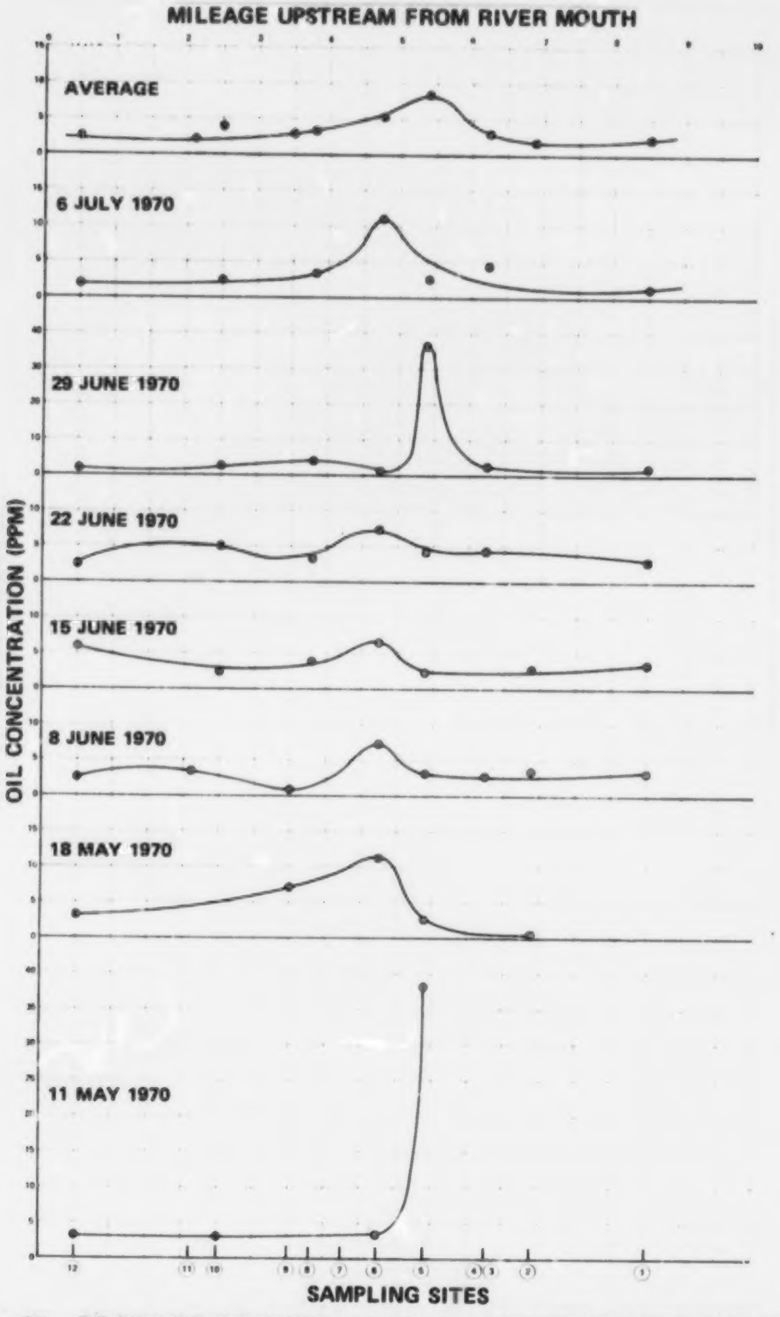


Figure 46 PROFILES OF BUFFALO RIVER BOTTOM-WATER BURDEN OF CHLOROFORM-EXTRACTABLE OILY POLLUTANTS

from its mouth. This 2-mile section of the River is the site of the heaviest concentration of industry; the sections of the River farther downstream and closer to the mouth are dominated by light industries and granaries.

One of the major concomitants of this high discharge of oil and organic chemical pollutants in the industrialized section is that it very severely depresses the dissolved oxygen content of the River. A later section of this report which discusses sampling and analysis effort undertaken in support of the pneumatic barrier evaluation (Reference 2) demonstrates that the dissolved oxygen concentrations even as far downstream as the site of the pneumatic barrier remained markedly low. The large increase in chemical oxygen demand, already noted, must be associated with the introduction of oxidizable pollutants which diminish the dissolved oxygen in a very rapid manner in this heavily industrialized sector of the River. Soluble organic dyes, many aniline-based, enter the River in this region and could be partially or mainly responsible for the increased COD.

Having isolated the heaviest concentration of oily pollutants in the Buffalo River to this reasonably short two-mile segment, an additional amount of sampling and analytical work was warranted to attempt a correlation of oil concentrations with depth in this segment. Figures 47 and 48 present vertical profiles of the chloroform-extractable matter at Sites 5 and 6 in the Buffalo River, which were the two major sampling points within this two-mile heavily polluted segment. These figures demonstrate both the very high concentration of oily pollutants near the surface and near the bottom at each of these sites and the much lower concentration in the bulk water flow between the first foot of the water surface and the last foot near the bottom. Thus, it can be seen that the augmentation of flow due to the Buffalo River Improvement Project is keeping the River bulk reasonably free between the surface and the bottom. The prevailing upriver winds couple to the surface pollutant layers and keep them "bottled up" in the upstream portion. Sedimentation of the pollutants on solids from industrial outfalls and general trapping of oils in the sediments are apparently not influenced by the augmented flow because of the basically laminar flow pattern in this slowly moving waterway. Even the higher flow is too low to scrub pollutants from the bottom sediments very rapidly. But as previously noted, over a period of a few years, the bottom sediments were noticeably "cleaner." The bottom layer of water is apparently also poorly mixed with the upper layers, accounting for the observed higher proportion of suspended or emulsified "oils" in this near-bottom zone.

Figure 49 presents infrared spectra of the complex oily pollutants typically found in high concentrations in the bottom waters (that is, at the 25-foot depth) of the industrial sector of the Buffalo River at Sites 5 and 6. It would not be precise to call these pollutants simply "oils." Rather, they are complex and noxious organic materials which must have been derived from the adjacent industries within this two-mile stretch.

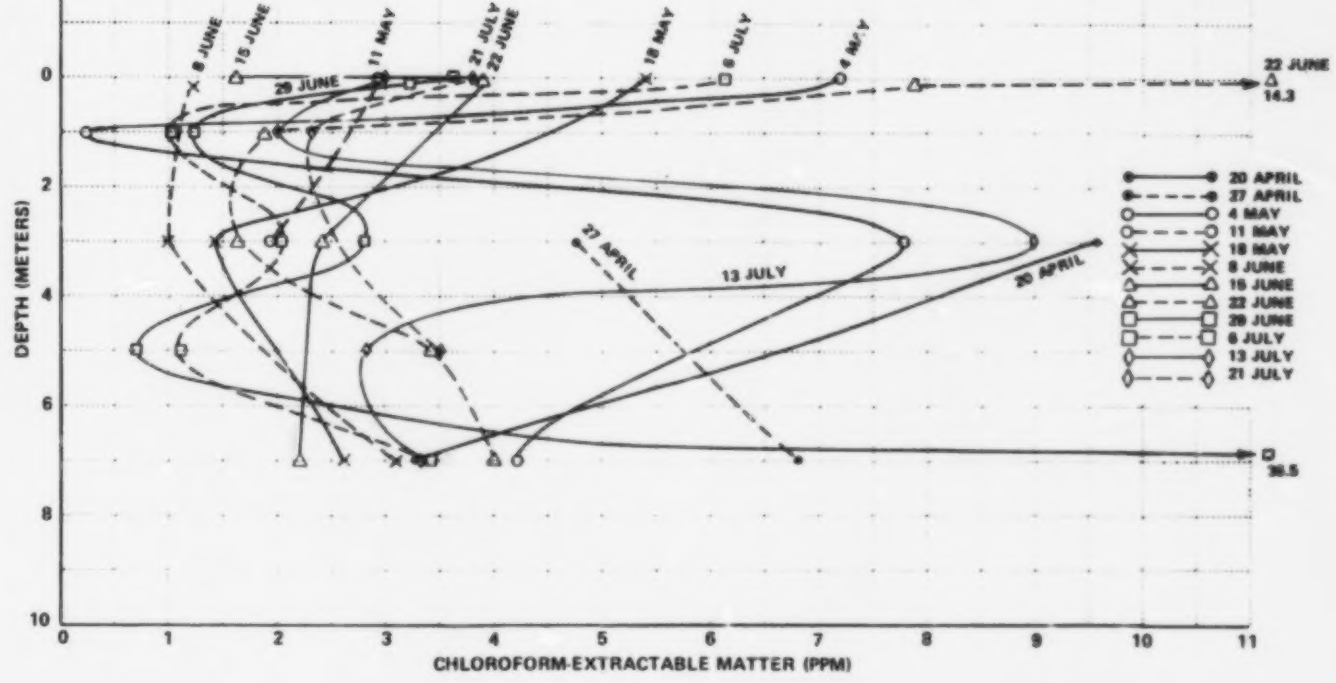


Figure 47 VERTICAL PROFILES OF CHLOROFORM EXTRACTABLES FOR SAMPLING SITE 5 (1970)

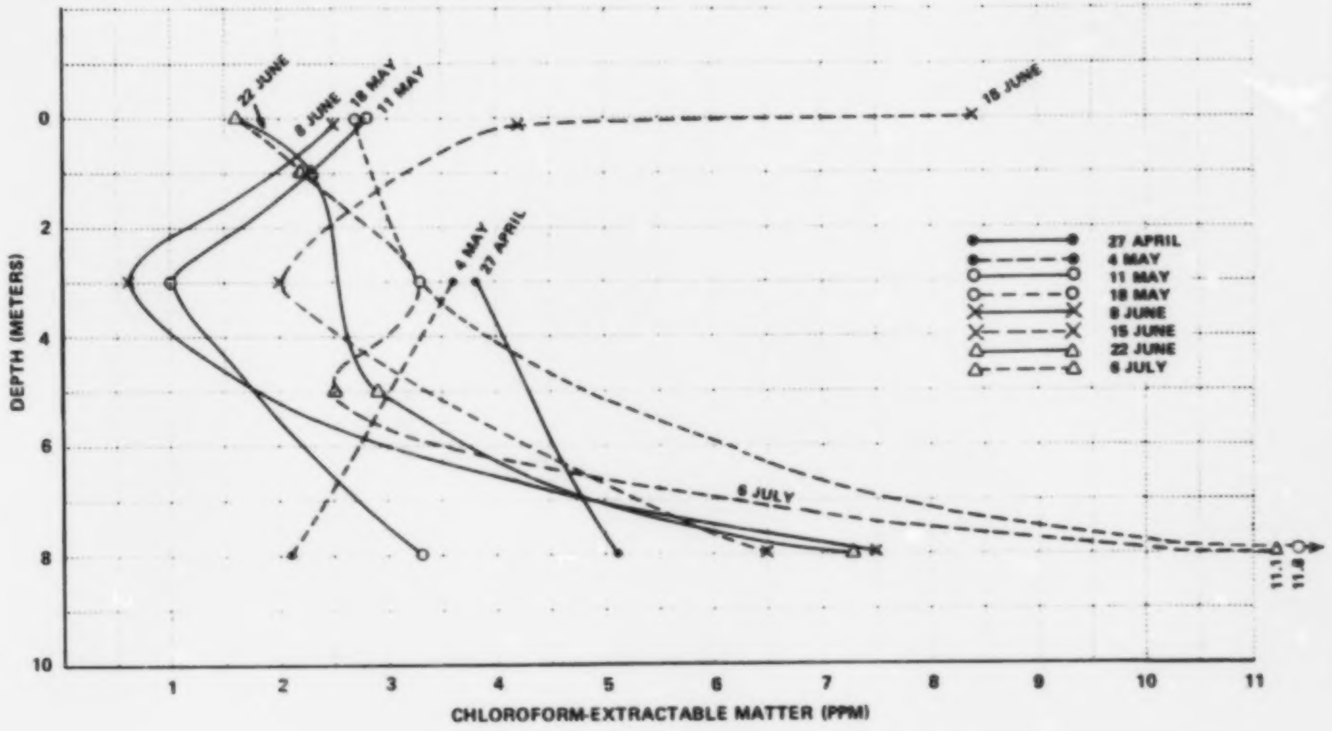


Figure 48 VERTICAL PROFILES OF CHLOROFORM EXTRACTABLES FOR SAMPLING SITE 6 (1970)

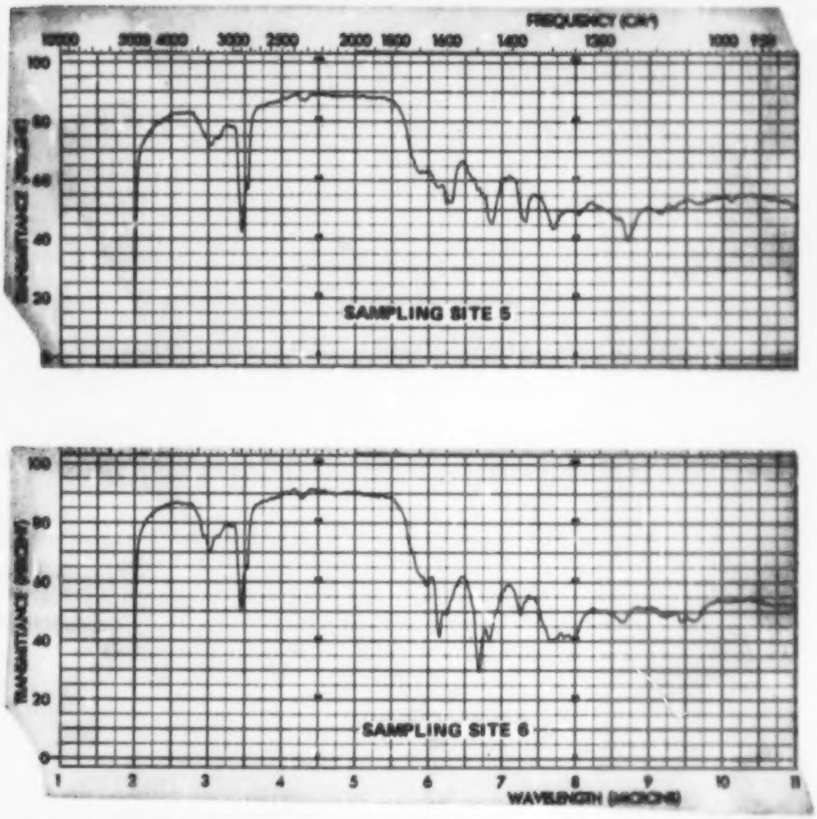


Figure 49 INFRARED SPECTRA OF THE COMPLEX OILY POLLUTANTS TYPICALLY FOUND IN HIGH CONCENTRATIONS IN THE BOTTOM WATERS (25 FOOT DEPTH) OF THE INDUSTRIAL SECTOR OF THE BUFFALO RIVER

RELATIONSHIP OF BULK WATER OIL CONCENTRATION TO THE RIVER DISCHARGE

It has been generally postulated that the concentration of oil in the bulk water of an industrial watercourse might be related to the discharge of the river on the days samples were taken. The Buffalo River itself does not contain a United States Geological Survey (USGS) gauging station. Two of the three tributaries to the River (Cazenovia Creek and Buffalo Creek) do have continuously recording USGS gauging stations near their confluence with the River. Mean daily flows for the days on which samples were obtained were provided to us from the Water Resources Division, New York District, United States Geological Survey, by Mr. Russell Wagner. Discharge data from the third tributary (Cayuga Creek) were not available but were estimated from mean flow records. We were also given access to the gauging stations on Cazenovia Creek and Buffalo Creek and to the discontinued gauging station on Cayuga Creek where our own measurements allowed us to spot check and confirm the reliability of the mean flow record data.

In addition to discharge from the tributaries, the Buffalo River flow is complicated by the continuous and occasionally variable inputs received from industries participating in the Buffalo River Improvement Project. During periods of low flow these inputs can contribute significantly to the net discharge of the River.

The first column of Table 8 records the combined mean daily discharge from the Buffalo River tributaries on the sampling dates during the 1970 season. The remaining columns in this table record the cumulative discharge at each sampling site when the discharge from the industries participating in the improvement project is added to the inflow discharge from the feeder streams. We are grateful to Richard Kressin of the Buffalo Sewer Authority for providing the rating tables from the cooling water project as an aid in preparing this table.

Figure 50 plots the measured oil concentrations in the bulk river water vs. mean daily flow and cumulative discharge from the industries participating in the cooling water project. In the topmost graph of Figure 50, a correlation, though perhaps not a significant correlation, is shown between the discharge and the oil concentration found in the surface screen samples (estimated to collect the top 1/60 inch of water). As shown, there is an apparent tendency for the oil concentration to diminish as the discharge is augmented. The further graphs in this figure plot the oil concentration vs. discharge for samples at the one-meter depth, in the three-to-five-meter depth range, and for the bottom water, respectively. Little or no correlation is evident between discharge and oil concentration beneath the immediate surface waters. Although one would expect that the oil concentration should decrease in these depth samples with the increasing discharge, due to the diluting effect of the additional water available, it appears that in the Buffalo River, the addition of fresh cooling water in the indus-

Table 8

MEAN DAILY DISCHARGE OF BUFFALO RIVER ON SAMPLING DATES
(DISCHARGES IN CUBIC FEET PER SECOND)

DATE (1970)	COMBINED DISCHARGE OF CAZENOVIA, CAYUGA, & BUFFALO CREEKS*	DISCHARGE AT SAMPLING SITE 1	DISCHARGE AT SAMPLING SITE 3	DISCHARGE AT SAMPLING SITE 5	DISCHARGE AT SAMPLING SITE 6	DISCHARGE AT SAMPLING SITE 8	DISCHARGE AT SAMPLING SITE 10	DISCHARGE AT SAMPLING SITE 12
27 APRIL	380	380	380	451	530	566	566	566
4 MAY	254	254	254	325	404	440	440	440
11 MAY	304	304	304	375	454	490	490	490
18 MAY	681	681	681	752	831	867	867	867
20 MAY	271	271	271	342	421	457	457	457
25 MAY	521	521	521	592	671	707	707	707
1 JUNE	140	140	140	211	290	326	326	326
8 JUNE	109	109	109	180	259	295	295	295
15 JUNE	92	92	92	163	242	278	278	278
22 JUNE	68	68	68	145	218	254	254	254
29 JUNE	75	75	75	152	225	261	261	261
6 JULY	59	59	59	136	209	245	245	245
13 JULY	86	86	86	157	236	272	272	272
20 JULY	394	394	394	465	544	580	580	580
1 AUGUST	235	235	235	306	385	421	421	421
25 AUGUST	64	64	64	135	214	250	250	250
31 AUGUST	106	106	106	177	239	275	275	275
8 SEPTEMBER	44	44	44	115	194	230	230	230
18 SEPTEMBER	164	164	164	195	314	350	350	350
30 SEPTEMBER	224	224	224	295	374	410	410	410
MEAN FOR SAMPLING DATES	214	214	214	283	363	399	399	399

*FLOW MEASUREMENTS WERE NOT MADE BY THE USGS ON CAYUGA CREEK IN 1970. CAYUGA CREEK CONTRIBUTES ~20% OF THE MEAN COMBINED FLOW OF BUFFALO RIVER TRIBUTARIES. THEREFORE, COMBINED FLOW OF CAZENOVIA AND BUFFALO CREEKS WAS INCREASED BY 20% TO REFLECT ESTIMATED FLOW INPUT OF CAYUGA CREEK.

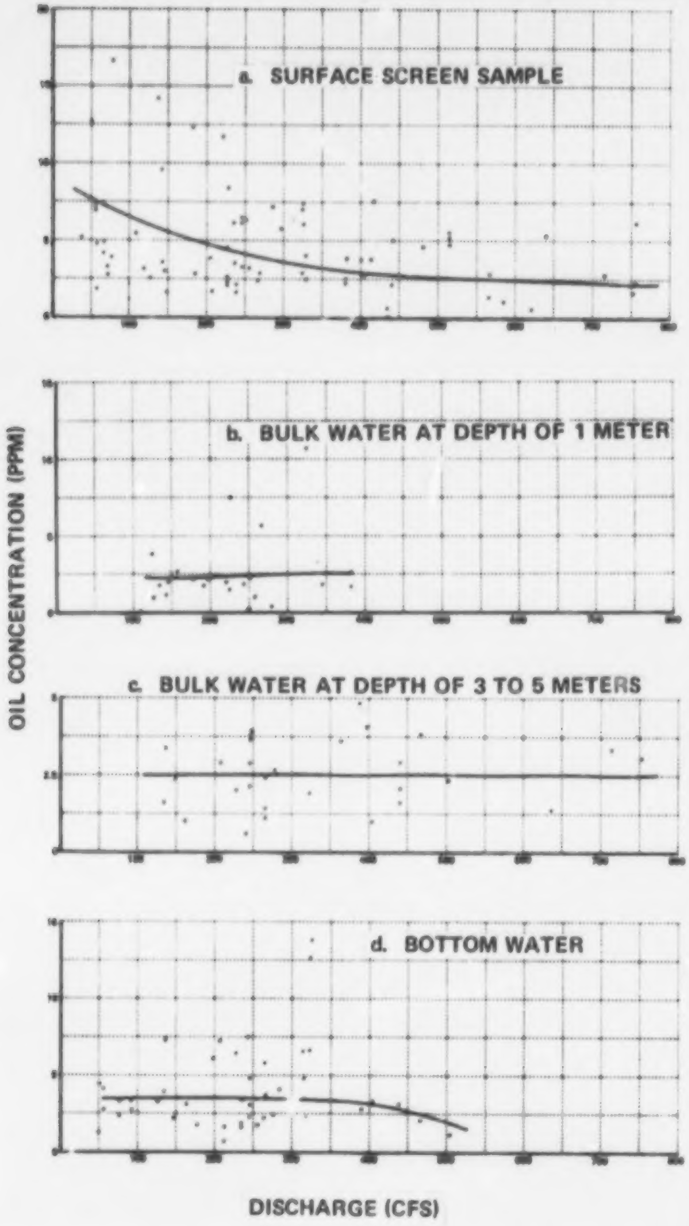


Figure 50 EFFECT OF STREAM DISCHARGE RATE ON OIL CONCENTRATION

trial sector is completely counteracted by the concurrent addition of oily effluents. The estimated 100,000,000 to 120,000,000 gallons per day augmentation of flow by the Buffalo River Improvement Project is probably the major factor in preventing a large build-up in oil concentration in the industrialized sector, but does not seem to be sufficient by itself to diminish it substantially.

DISCUSSION OF DATA ON BULK WATER OIL CONTENT

The average oil concentrations (in ppm) in each layer sampled during the period April-October, 1970 have been determined and are included in Tables 9, 10, 11, and 12 to aid in the following discussion.

As previously noted, there was considerable variation in the measured oil concentration from week to week. The greatest variation noted throughout two years of sampling occurred in bulk river water at the river bottom where the variation was from about 0 ppm to, on some occasions, 40 ppm. The rather high concentration for the near-bottom samples was not frequently observed, and it is suggested that some stirring up of oily sediments from the bottom layers may have occurred during the sample taking process. Inspection of the tables will show that, over the 1970 sampling period, the greatest oil concentration generally was in the surface waters (as has been previously shown graphically). In the sector of the river containing predominantly heavy industry, however, the bottom water samples often contained more suspended or emulsified oil than did the surface waters, probably reflecting the adsorption of the "oily" pollutants onto sedimenting particles discarded in many of the industrial effluents. The average concentration of oil, again as shown earlier graphically, decreased at the one-meter and three-to-five-meter depths. In the industrial sector, the average concentration was slightly greater at the three-to-five-meter depth; in the granary sector, the situation was reversed with the greater oil concentrations generally occurring near the surface at the one-meter depth. The figures already presented showed that the concentration of oil present in the surface and bottom waters of the Buffalo River increased markedly as one proceeded from the upper river system and the feeder tributaries to the industrial sector. The oil concentration then decreased as the river proceeded towards its mouth via the granary and light industry segments of the River. The concentration of oil present in the bulk water volume at the one-meter depth increased generally from the industrialized sector to the granary sector while the concentration of water at slightly greater depths (three to five meters) tended to decrease slightly as the river flowed from the industrialized sector. There is, of course, considerable daily variation from the pattern illustrated in any one day in surface or bulk water or bottom water profiles. No definite conclusions can be drawn until these observations can be extended and confirmed.

Table 9

CHLOROFORM-EXTRACTABLE MATTER (PPM) IN BULK WATER AT SURFACE

DATE (1970)	SAMPLING SITE NO.						
	1	3	5	6	8	10	12
4 MAY	—	—	7.2	—	—	—	—
11 MAY	3.1	—	2.9	2.8	5.0	—	2.1
18 MAY	1.3	2.9	5.4	2.7	1.6	2.2	6.1
20 MAY	4.5	2.4	5.8	3.8	7.6	3.8	—
25 MAY	0.6	0.0	2.6	1.0	—	—	0.5
1 JUNE	3.1	—	<1.0	0	—	—	—
15 JUNE	3.9	16.7	1.6	8.4	2.4	2.5	1.1
22 JUNE	4.8	1.8	14.3	1.6	6.1	3.3	6.5
29 JUNE	4.2	4.9	3.6	—	4.0	8.0	6.2
6 JULY	—	—	6.1	1.6	—	2.6	—
13 JULY	2.7	3.3	3.0	11.7	4.6	6.3	3.6
21 JULY	2.5	4.1	3.8	4.6	5.2	4.7	5.5
11 AUGUST	—	—	2.9	10.6	—	2.5	2.3
18 AUGUST	—	—	—	3.8	—	0.1	—
25 AUGUST	7.3	7.1	2.5	3.7	2.1	3.2	—
31 AUGUST	1.4	—	5.9	3.3	4.6	6.9	—
8 SEPTEMBER	—	5.1	5.5	2.8	—	2.3	2.1
18 SEPTEMBER	—	9.6	12.4	—	7.0	7.9	6.0
30 SEPTEMBER	—	—	11.6	19.6	12.0	12.0	—
AVERAGE	3.3	5.2	5.4	5.1	5.0	4.5	3.8

Table 10

CHLOROFORM-EXTRACTABLE MATTER (PPM) IN BULK WATER AT DEPTH OF 1 METER

DATE (1970)	SAMPLING SITE NO.				
	5	6	8	10	12
22 JUNE	1.8	2.3	—	1.9	—
29 JUNE	1.2	—	0.1	—	—
6 JULY	1.0	2.2	—	—	—
13 JULY	2.0	—	2.3	—	—
31 JULY	2.3	—	—	—	—
11 AUGUST	—	1.8	2.6	—	1.6
18 AUGUST	—	0.8	0.2	0.4	0.5
25 AUGUST	3.8	—	—	—	—
31 AUGUST	2.7	2.0	1.0	5.6	—
8 SEPTEMBER	0.0	1.7	—	1.5	7.8
18 SEPTEMBER	2.2	—	11.8	—	—
AVERAGE	1.7	1.8	3.0	2.5	3.3

Table 11

CHLOROFORM-EXTRACTABLE MATTER (PPM) IN BULK WATER AT DEPTHS OF 3, 4, AND 5 METERS

DATE (1970)	SAMPLING SITE NO./DEPTHS (METERS)														
	5			6			8			10			12		
	3	4	5	3	4	5	3	4	5	3	4	5	3	4	5
27 APRIL	4.8	--	--	3.8	--	--	--	--	--	--	--	--	2.3	--	--
4 MAY	7.8	--	--	3.6	--	--	--	--	--	--	--	--	4.1	--	--
11 MAY	1.9	--	--	1.0	--	--	1.6	--	--	2.1	--	--	2.9	--	--
18 MAY	1.4	--	--	3.3	--	--	--	--	--	--	--	--	3.1	--	--
1 JUNE	0.0	--	--	0.0	--	--	--	--	--	--	--	--	0.0	--	--
8 JUNE	1.0	--	--	0.6	--	--	--	--	--	--	--	--	2.6	--	--
15 JUNE	2.4	--	--	2.0	--	--	2.4	--	--	1.6	--	--	1.1	--	--
22 JUNE	1.6	--	3.4	--	--	2.9	3.8	--	--	--	--	3.6	2.1	--	2.7
29 JUNE	2.8	--	0.7	3.6	--	--	0.8	--	0.7	1.4	--	--	1.6	--	--
6 JULY	2.0	--	1.1	3.3	--	2.5	--	--	--	3.0	--	1.4	--	--	--
13 JULY	9.0	--	2.8	--	--	--	2.2	--	--	--	--	--	--	--	--
21 JULY	--	--	3.5	--	--	--	6.2	--	--	--	--	--	--	--	--
28 JULY	--	--	2.6	--	--	6.0	--	--	--	0.2	--	2.0	--	--	--
11 AUGUST	1.7	--	--	--	--	1.9	--	--	--	1.8	--	2.4	--	--	0.9
18 AUGUST	--	--	--	--	1.7	--	--	1.1	--	--	1.6	--	--	1.2	--
25 AUGUST	--	--	--	--	--	--	--	0.2	--	--	--	--	--	--	--
31 AUGUST	--	0.9	--	--	0.6	--	--	1.0	--	--	--	--	--	--	--
8 SEPTEMBER	--	0.0	--	--	1.3	--	--	--	--	--	0.2	--	--	4.5	--
18 SEPTEMBER	--	6.0	--	--	--	--	--	9.0	--	--	6.2	--	--	--	--
AVERAGE	--	3.0	--	--	2.3	--	--	2.5	--	--	2.1	--	--	2.2	--

Table 12

CHLOROFORM-EXTRACTABLE MATTER (PPM) IN BULK WATER AT RIVER BOTTOM

DATE (1970)	SAMPLING SITE NO.						
	1	3	5	6	8	10	12
20 APRIL	—	1.5	3.3	5.1	—	—	—
27 APRIL	4.9	3.5	—	2.1	—	—	1.2
4 MAY	1.7	0.8	4.2	—	—	—	2.9
11 MAY	1.7	—	38.2	3.3	—	—	3.1
18 MAY	$<$1.0	1.9	2.6	11.3	—	2.9	2.6
1 JUNE	5.8	—	—	0	—	—	$<$1.0
8 JUNE	3.4	2.8	3.1	7.5	—	—	2.5
15 JUNE	3.4	2.9	2.2	6.5	3.7	2.2	5.8
22 JUNE	2.8	4.1	4.0	7.3	3.1	4.9	2.4
29 JUNE	—	2.1	36.5	1.0	3.7	2.5	1.8
6 JULY	1.3	4.5	3.4	11.1	3.4	3.5	1.8
11 AUGUST	—	—	2.8	8.8	—	3.1	2.4
18 AUGUST	—	—	—	2.8	—	3.1	4.2
25 AUGUST	3.5	0.5	6.8	2.5	1.9	3.5	—
31 AUGUST	5.1	—	1.7	2.4	3.1	2.7	—
8 SEPTEMBER	—	1.4	0.0	9.4	—	10.8	3.8
18 SEPTEMBER	—	7.8	1.8	—	13.8	6.6	13.2
30 SEPTEMBER	—	—	13.2	2.6	$<$1.0	$<$1.0	—
AVERAGE	3.1	2.8	7.9	5.2	4.2	3.9	3.4

ESTIMATION OF THE OIL TRANSPORTED IN THE BULK WATER OF THE BUFFALO RIVER

Estimates of the quantity of oil discharged daily from the upper river system, the industrial sector, and the granary sector were made by selecting representative concentrations from the tables just presented. An amount of oil discharged daily was computed using the mean flow data for the upper river, the industrial sector, and the granary sector as presented in Table 8. The following sample calculations will make it evident that the amount of oil in the surface water, although it is the most obvious and publicly apparent oil nuisance, is small in quantity when compared with the amount of oil carried in the bulk water phase at greater depths.

The following calculations consider a one foot square column of the river, in the industrial or granary sector, as having layered vertical cross sections as shown in Figure 51. The layering depicted there is, of course, arbitrary and based solely on our sampling routine. In the following calculations, depths have been converted to feet from meters to facilitate computation. In Figure 51, the depths at which samples were routinely taken is shown by the dashed-line arrows. Representative concentrations for the various layers, which were used in these calculations, and the computed quantity of oil in each layer are given in Table 13. The weight of oil in each layer was computed by the following formula: the weight of oil per square foot in each layer depth equals the volume of the layer in cubic feet times the density of water (62.4 lb per cubic foot) times the oil concentration (in lb per lb). The total amount of oil in about 26 cubic feet of water in the industrial or granary sector was found by summing the amounts in individual layers, and amounted to about 49×10^{-4} lb for the industrial sector and about 42×10^{-4} lb for the granary sector. Each cubic foot of water discharged through the industrial sector typically contained about 1.9×10^{-4} lb of oil and each cubic foot in the granary sector typically contained about 1.6×10^{-4} lb of oil. The mean daily discharge of oil through the industrial or granary sectors could thus be estimated as follows: the mean daily discharge of oil = the mean water discharge (in cubic feet per second) x the oil concentration (in pounds per cubic foot) x 3600 seconds per hour x 24 hours per day. The mean daily discharge of oil through the industrial sector is estimated to be 325 cubic feet per second x 1.9×10^{-4} pounds per cubic foot x 8.64×10^{4} seconds per day, or about 5300 pounds per day.

The mean daily discharge of oil through the granary sector (400 cubic feet per second x 1.6×10^{-4} pound per cubic foot) equalled about 5500 pounds per day.

The Buffalo River, in both the industrial and granary sectors, is dredged by the Army Corps of Engineers to a depth of eight meters or about 26 feet. The upper river system beyond the industrialized sector is not dredged and is much shallower. The average depth of water in the upper river during the sampling periods of 1969 and 1970 was about

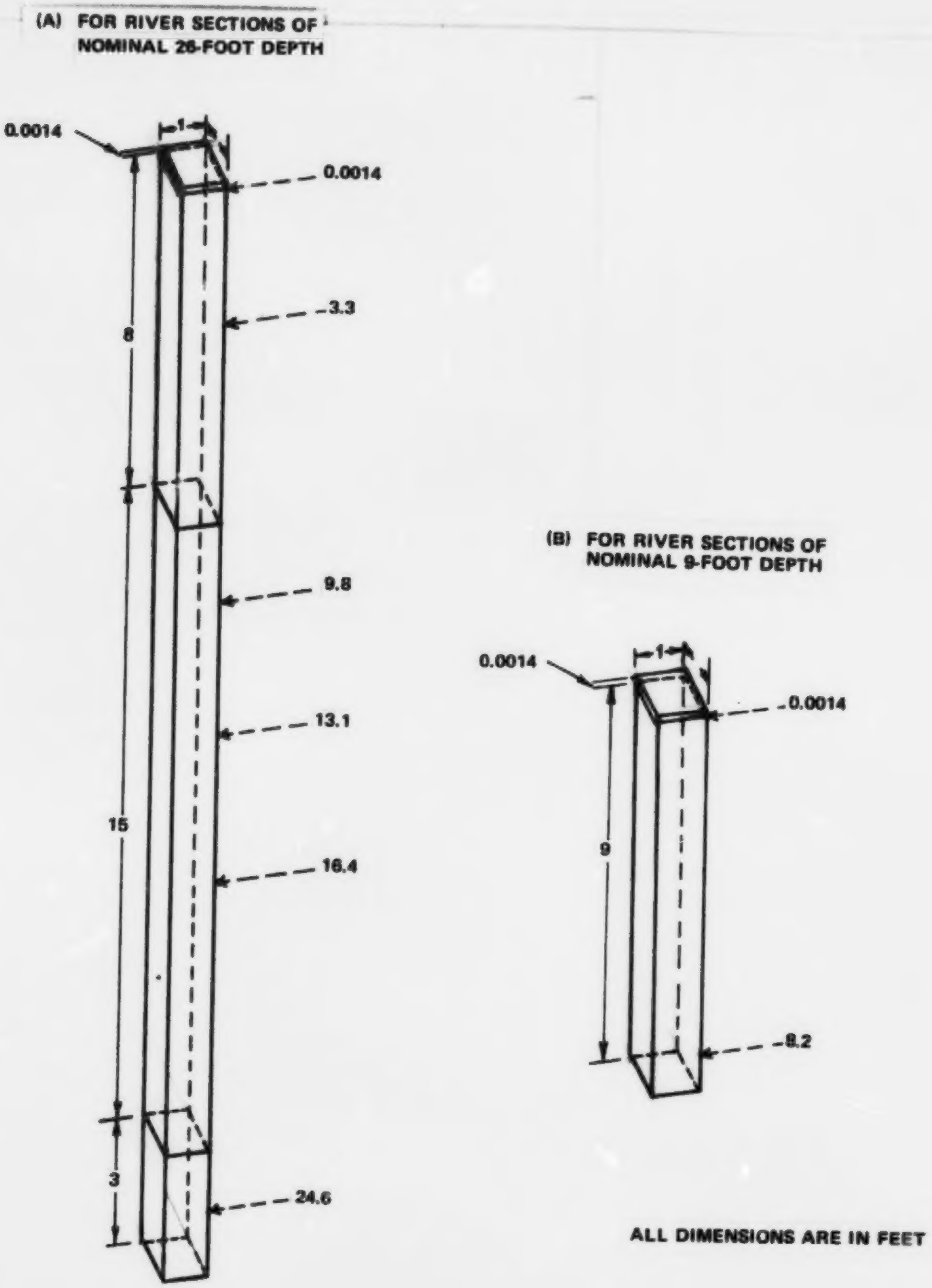

(A) FOR RIVER SECTIONS OF NOMINAL 26-FOOT DEPTH
0.0014
1
0.0014
3.3
8
9.8
13.1
15
16.4
3
24.6
(B) FOR RIVER SECTIONS OF NOMINAL 9-FOOT DEPTH
0.0014
1
0.0014
9
8.2
ALL DIMENSIONS ARE IN FEET

Figure 51 VERTICAL SPACING OF RIVER LAYERS FOR COMPUTING OIL CONCENTRATION

Table 13

CHLOROFORM-EXTRACTABLE MATTER IN BULK WATER OF INDUSTRIAL AND GRANARY SECTORS

LAYER DEPTH (ft)	INDUSTRIAL SECTOR		GRANARY SECTOR	
	CONCENTRATION (PPM)	QUANTITY (lb)	CONCENTRATION (PPM)	QUANTITY (lb)
0.0 – 0.0014	5	44×10^{-8}	5	44×10^{-8}
0.0014 – 8	2	10×10^{-4}	3	15×10^{-4}
8 – 23.0	3	28×10^{-4}	2	19×10^{-4}
23.0 – 26.	6	11×10^{-4}	4	8×10^{-4}
0.0 – 26.	--	49×10^{-4}	--	42×10^{-4}

9 feet. The layered cross section for this sector along with the sampling depths routinely chosen is given in Figure 51. Representative concentrations for the surface and sub-surface depths, as read from the previous tables and figures, were chosen as 5 ppm for the surface and 3 ppm for the bulk water. This translates to 4 x 10-8 lb of oil in the surface layer and approximately 17 x 10^{-4} lb in the sub-surface layer all the way down to the bottom at the nine foot depth. The amount of oil estimated to be present in the mean daily discharge above the industrialized section, over the sampling period, was therefore computed as approximately 3500 lb, representing contributions from scattered communities and industries (including some heavy manufacturing and lubricant plants) along the twenty-mile or so transit of the stream before it becomes defined as the Buffalo River. The amount of oil found in the industrial sector, in excess of the quantity flowing from the upper river system into it, may then be estimated as 1800 lb daily (5300 - 3500). As noted above, the amounts of oil discharged daily through the industrial and granary sectors are estimated to be 5300 lb and 5500 lb, respectively. These sample calculations of the amount of oil discharged daily through the various sectors of the river are not indicative of the amount of oil present in the total riverine environment. As documented in other sections of this report, very large quantities of oil are present in the bottom sediments and on the river banks. In addition, there are stagnant pools of very thick floating surface deposits along naturally sheltered bank areas and in natural traps along the river line. The Environmental Protection Agency's "Lake Erie Report," issued in 1968, estimated an input of over 12,000 lb of oil daily into the Buffalo River from only three major sources; other sources of oily pollutants were identified but quantitative amounts were not assigned to these discharges.

The amount of oil discharged daily from these industrial sources may have, indeed, diminished since the issuance of the Lake Erie Report in 1968, but it is our current estimate that at least 6500 lb of oil (12000 - 5500) are deposited daily in the sediments and on the banks of the Buffalo River. Much of the oil released into the Buffalo River waters in the industrial sector is carried upstream, as a thick and publicly apparent gross oil slick, by the prevailing southwest winds and deposited in quiescent pools or on stream banks. Collection and measurement of shore oil deposition and thick surface films is documented in other sections of this report.

WATER TEMPERATURES AND DISSOLVED OXYGEN PROFILES

Although records of the water temperature and of quantity of dissolved oxygen in this major industrial watercourse were peripheral to the major interests of this program in oil pollution, the data are nonetheless of substantial interest as general indicators of the overall stream quality. Table 14 reports the Buffalo River water temperatures at an eight-inch depth over the 1970 season. The major portion of these data are plotted in Figure 52. It can be noted from both the table and the figure that there is a dramatic increase in water temperature throughout spring and summer and even into the fall season, as the water is slowed in its approaches to the dredged deeper portion. In the industrial section, it also receives relatively warmer effluents from the industries.

Figure 52 illustrates this temperature hump graphically, and also shows the general constancy of the high temperature right out to the mouth of the river at Lake Erie over a two-month to three-month period. The temperature regularly increased over the period from April through mid-July 1970, and then, after an erratic up and down fluctuation in July and August, began to decrease in a regular fashion during September.

The dissolved oxygen in the Buffalo River waters was also measured routinely early in the 1970 sampling program. Figure 53 shows, for example, sample vertical profiles of the dissolved oxygen content which were taken at 6 of the 12 regular sampling sites. As indicated in this figure, and as was found throughout the program, there was a relatively constant concentration of dissolved oxygen throughout the depth of the river.

Figure 54 plots the dissolved oxygen measured as a function of downstream distance for the water immediately below the surface. As seen in this figure, the dissolved oxygen content of this surface water decreases abruptly as the water enters into the industrial section. The oxygen content stays at this very low value until the stream approaches Lake Erie where some mixing with the highly oxygenated lake water is always noted. At the water temperatures involved, the observed oxygen concentrations in the inflow waters usually represented

Table 14

BUFFALO RIVER WATER TEMPERATURES AT 8-INCH DEPTH

SAMPLING SITE NO.	DATES (1970) AND TEMPERATURES (°F)													
	18 MAY	20 MAY	25 MAY	1 JUNE	8 JUNE	15 JUNE	22 JUNE	29 JUNE	6 JULY	13 JULY	21 JULY	28 JULY	18 SEPT	30 SEPT
1	50.3	63.5	59.6	72.3	69.5	72.2	65.8	69.2	71.0	76.0		79.9		
2	53.0		60.4	72.8	68.8									
3		65.5	60.7	73.0	70.2	74.2	72.8	73.5	79.2	84.0	66.0			
4	53.5													
5	57.5	68.3	68.0	74.6	74.2	77.0	78.4	78.3	82.2	84.0	72.0	86.8	77.0	70.0
6	60.0	68.3	69.0	75.0	75.2	75.2	78.0	77.0	79.7	84.0	75.0	86.2		
7	60.5		68.5	71.3										
8	58.0	68.2	68.2	71.8		73.8	75.6	75.4	79.5	81.8	73.0			67.0
9	59.0		68.7	72.8	73.3									
10	58.0	61.5	68.0	71.0		71.0	73.7	74.6	77.0	81.7	75.0	80.8		66.0
11			67.4	69.2	73.0									
MICH. AVE. (AIR BARRIER)	59.0	60.9	67.9	68.6	70.2	68.2	72.5	71.7						
12	58.5		62.9	69.0	73.5	66.3	61.5	69.8	73.7	75.2	74.0			

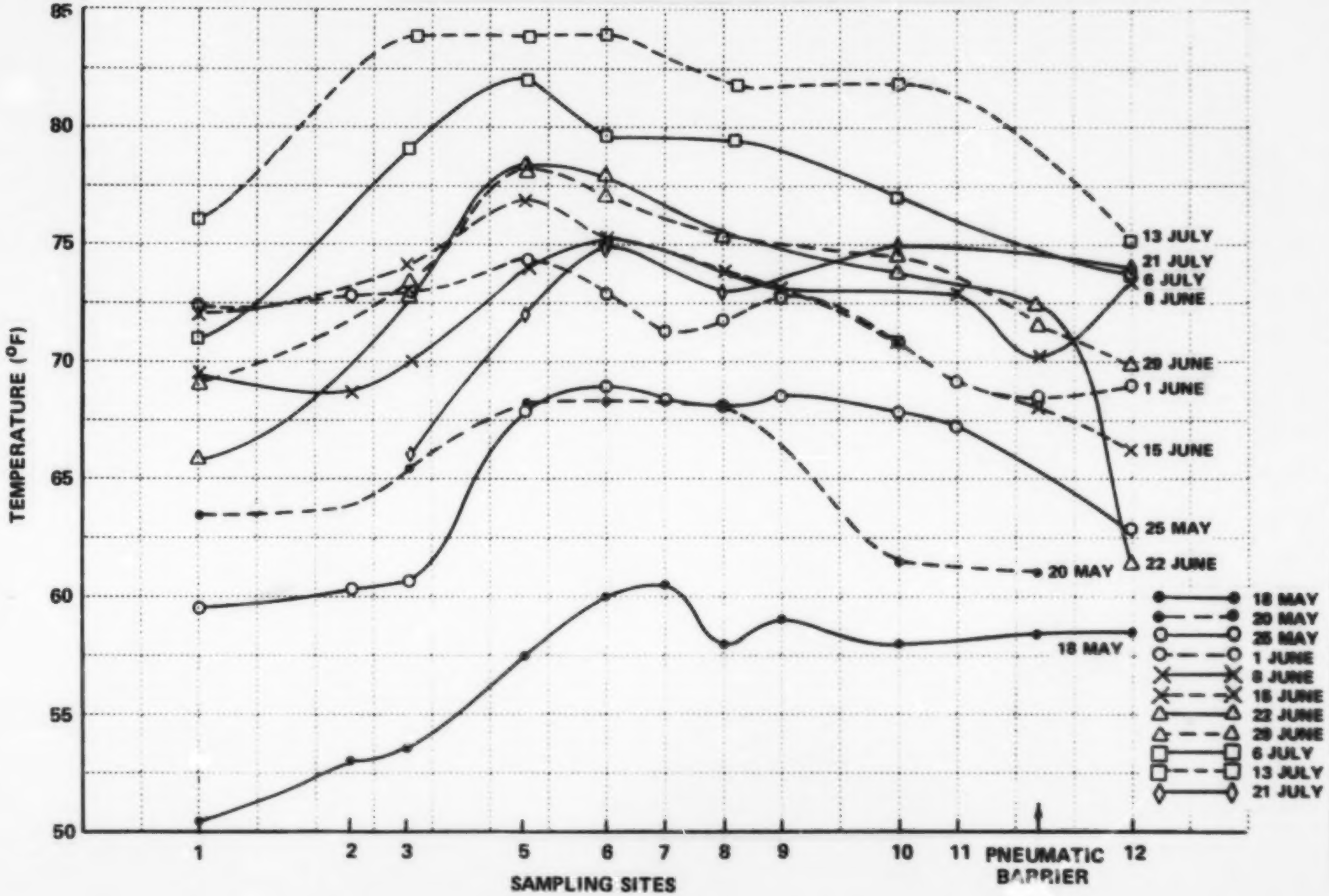


Figure 52 WATER TEMPERATURE AT DEPTH OF 8 INCHES

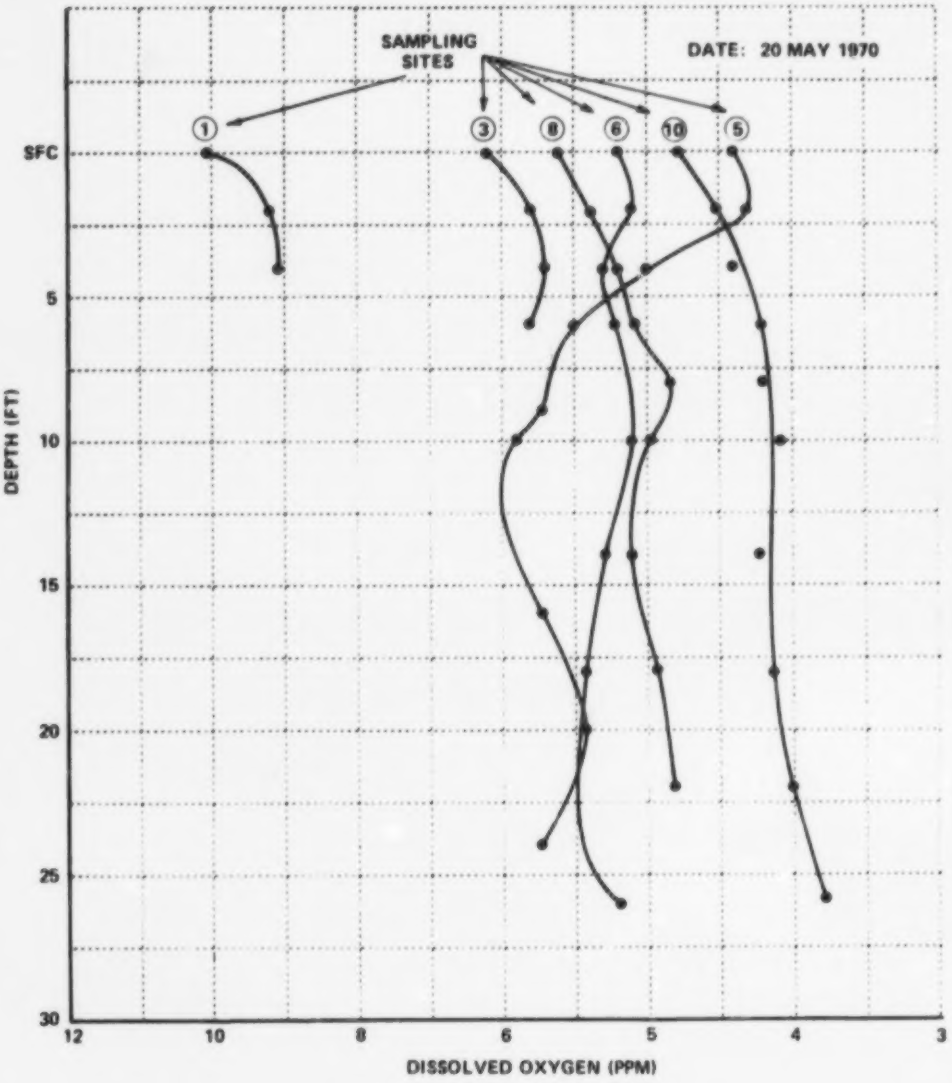


Figure 53 DISSOLVED-OXYGEN PROFILES

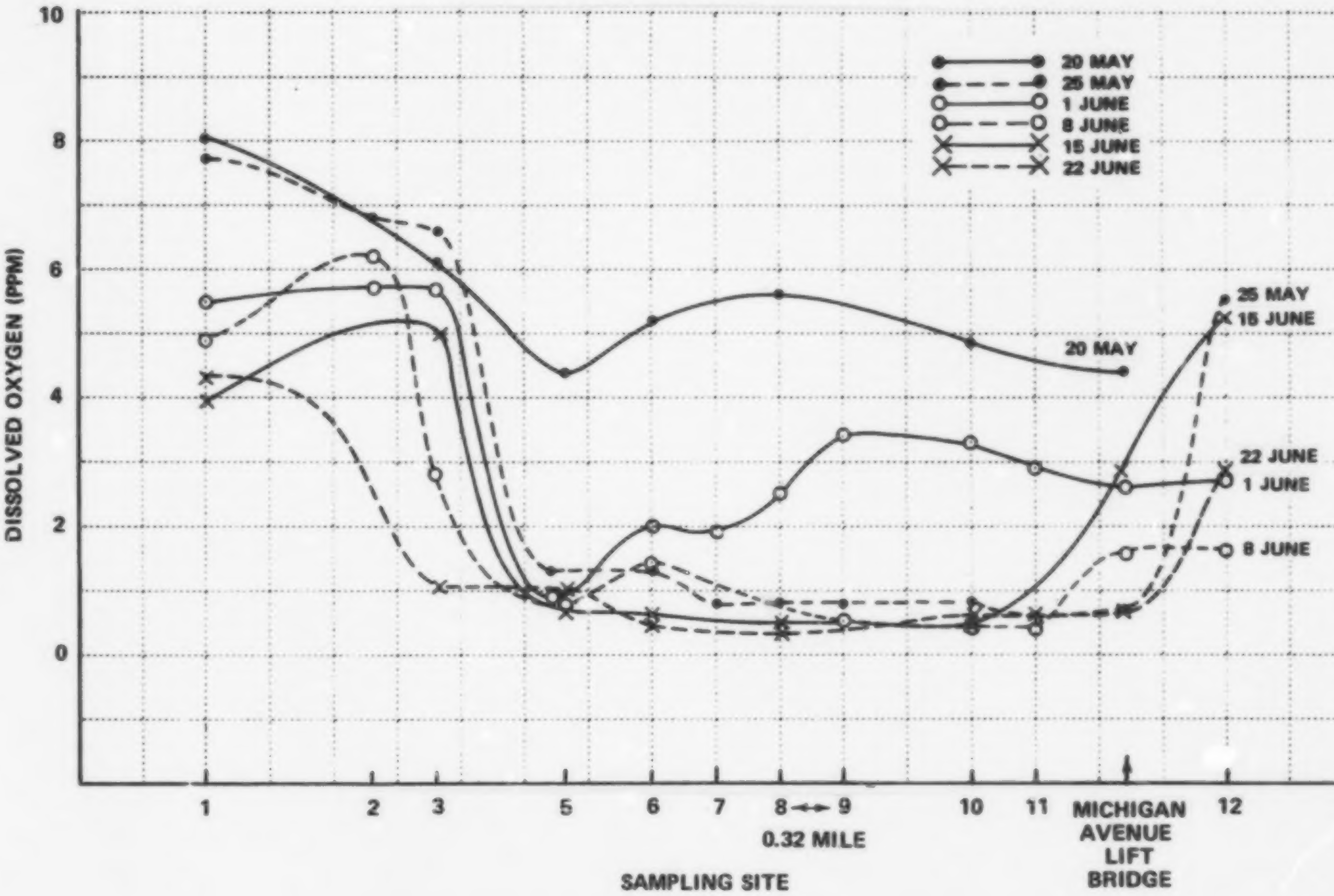


Figure 54 DISSOLVED-OXYGEN CONTENT OF SURFACE WATER

about 50% saturation and very rapidly dropped essentially to zero saturation in the industrial sector.

Figure 55 plots the measured dissolved oxygen at five different sites in the Buffalo River vs. time for the 1970 sampling program. It was discovered that, by the end of June, the dissolved oxygen values measured, except for the inflow waters, had dropped to essentially zero in all instances and at this point the oxygen-measurement program was terminated.

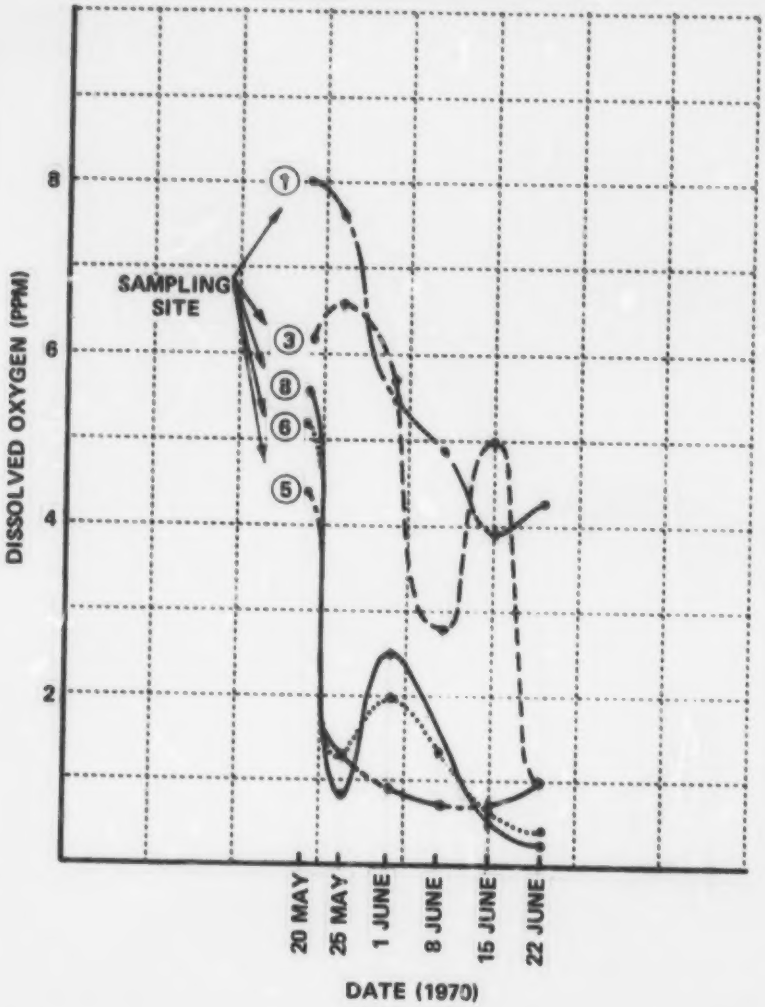


Figure 55 DISSOLVED-OXYGEN CONTENT VS. TIME

CHARACTERIZATION OF THE BOTTOM SEDIMENTS IN THE BUFFALO RIVER

Approximately 25 samples of Buffalo River bottom sediments were collected and analyzed during 1970 in accordance with the procedures described earlier in the sampling and analytical sections. Table 15 summarizes the concentrations of chloroform extractable materials found at the chosen sample points. The obvious variability of the data collected in Table XV caused a general limitation of sampling and analytical effort in this phase of the program. For example, on one given date when three separate bottom sediment samples were taken one next to the other, within minutes of one another, in the same location in the heavily industrialized section of the Buffalo River, the concentrations of chloroform-extractable matter were in the first sample 0.23%, in the second sample 0.11%, and in the third sample 0.50%. Superposed on this quantitative variability in the organics trapped in the bottom sediments, was the qualitative variability of the organic materials. This was true of the sediments even at the same location, and certainly among different locations along the course of the river. Figure 56, for example, shows typical infrared spectra characterizing oily pollutants trapped in bottom sediments of the Buffalo River. Trace A in this figure represents the "oils" trapped in the sediment at the mouth of the Buffalo River. Although there is some spectral evidence of oxygenated hydrocarbons, the spectrum is reasonably straightforward in indicating mainly oils in the traditional sense (that is, essentially aliphatic hydrocarbons). Traces B, C, and D in Figure 56, on the other hand, are infrared spectra representative of the organic extracts from the three samples mentioned above, which were taken side by side at the same heavily industrialized site in the Buffalo River. They are considerably different from one another, even to the stage of containing completely new peaks in certain of the spectra not found in the companion samples collected within the same square meter or so of the river bottom.

Figure 57 presents an infrared spectrum typical of "oily" pollutants suspended in the water column immediately above the sediment samples collected from the heavily industrialized Buffalo River sector. When such cross-comparative sampling was completed, it was seen that the pollutant burden in the Buffalo River sediments at most locations was quite diverse. Sedimentation of these suspended pollutants has apparently been very non-uniform.

Although the individual data points thus acquired showed extreme variability, an average of data collected over the entire sampling season of 1970 at each sampling location does show a correlation with the intensity of industrial activity along the shoreline. That is, the river bottom burden of organics trapped in the sediments is greatest in the heavily industrialized section of the River (in the two-mile section previously discussed). Figure 58 plots the average chloroform-extractable matter (in percent) in the bottom sediments vs. mileage along the Buffalo River from its mouth. This figure vividly

Table 15

PERCENT "OIL" EXTRACTABLE FROM BOTTOM SEDIMENTS AT VARIOUS BUFFALO RIVER SITES ON VARIOUS DATES

(CONTENT IN %)

DATE (1970)	SAMPLING SITE NO.								
	1	3	4	5	6	8	9	10	12
20 APRIL	0.3			9.8					
27 APRIL				0.26	1.2		0.70		0.23
4 MAY			0.05	0.11	0.65		0.34		
11 MAY		STONE		0.57	1.01	0.05		0.61	0.58
11 JULY				0.76	1.27	STONES 0.02		0.53	
18 SEPT		0.20		0.48					0.85
AVERAGE	0.3	0.2	0.05	1.43	1.03	0.03	0.52	0.57	0.55

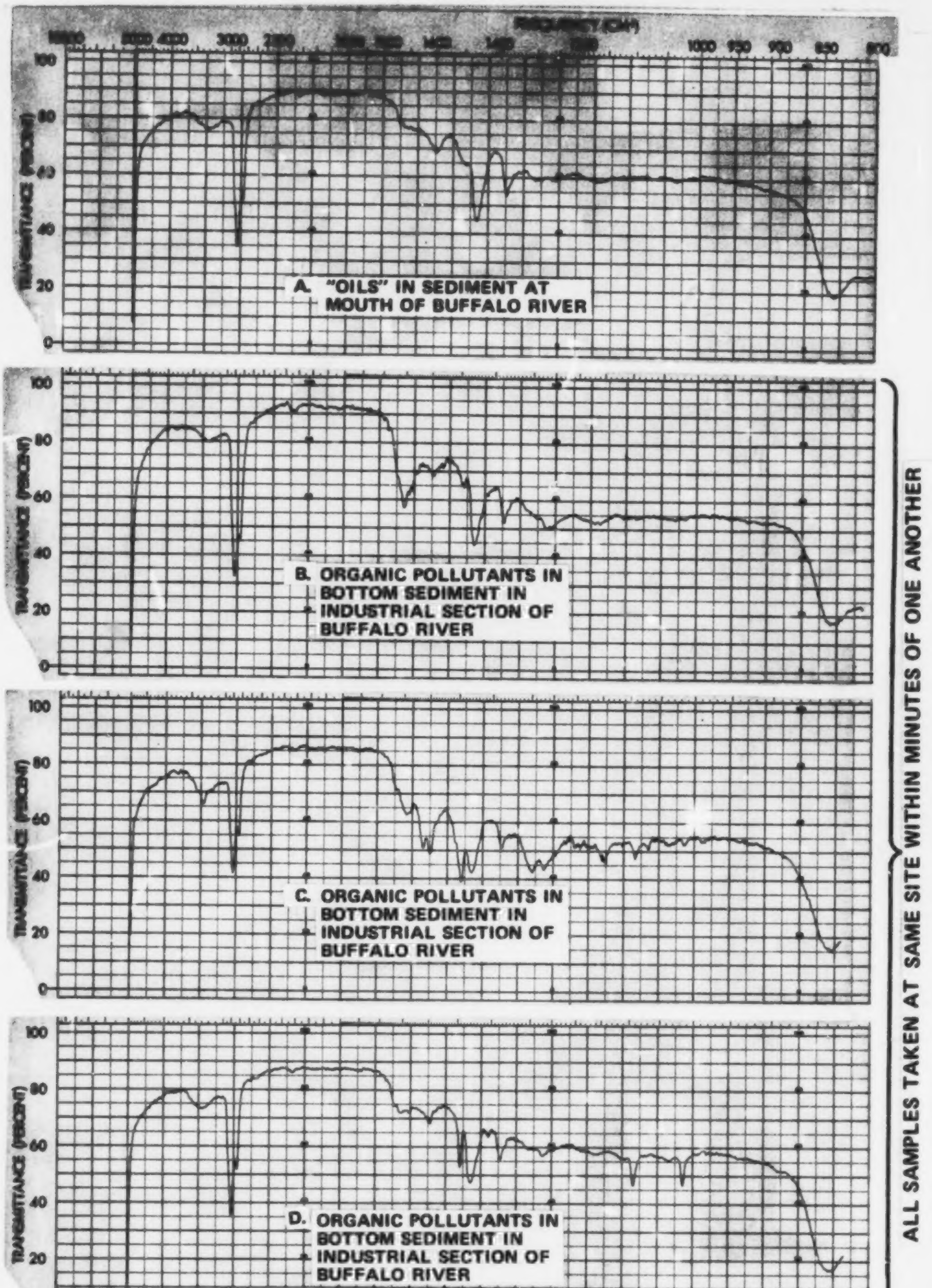


Figure 56 INFRARED SPECTRA CHARACTERIZING THE "OILY" POLLUTANTS TRAPPED IN THE BOTTOM SEDIMENTS OF THE BUFFALO RIVER

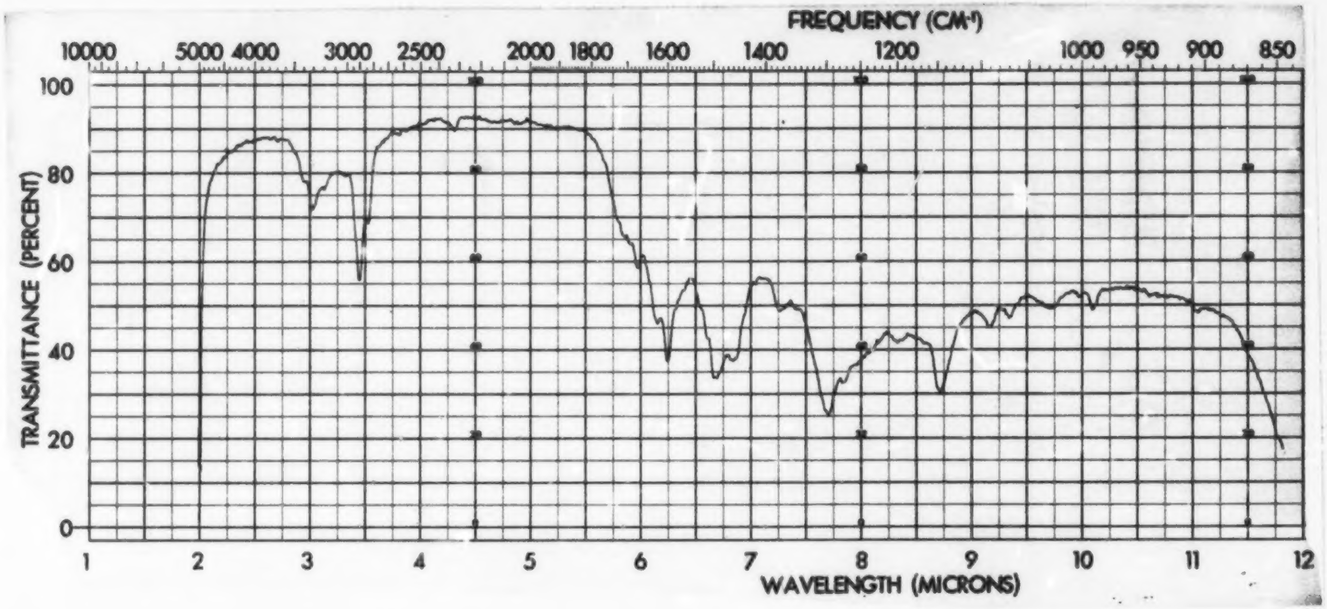


Figure 57 INFRARED SPECTRUM OF "OILY" POLLUTANTS SUSPENDED IN WATER COLUMN ABOVE SEDIMENT SAMPLES COLLECTED FROM HEAVILY INDUSTRIALIZED BUFFALO RIVER SECTOR

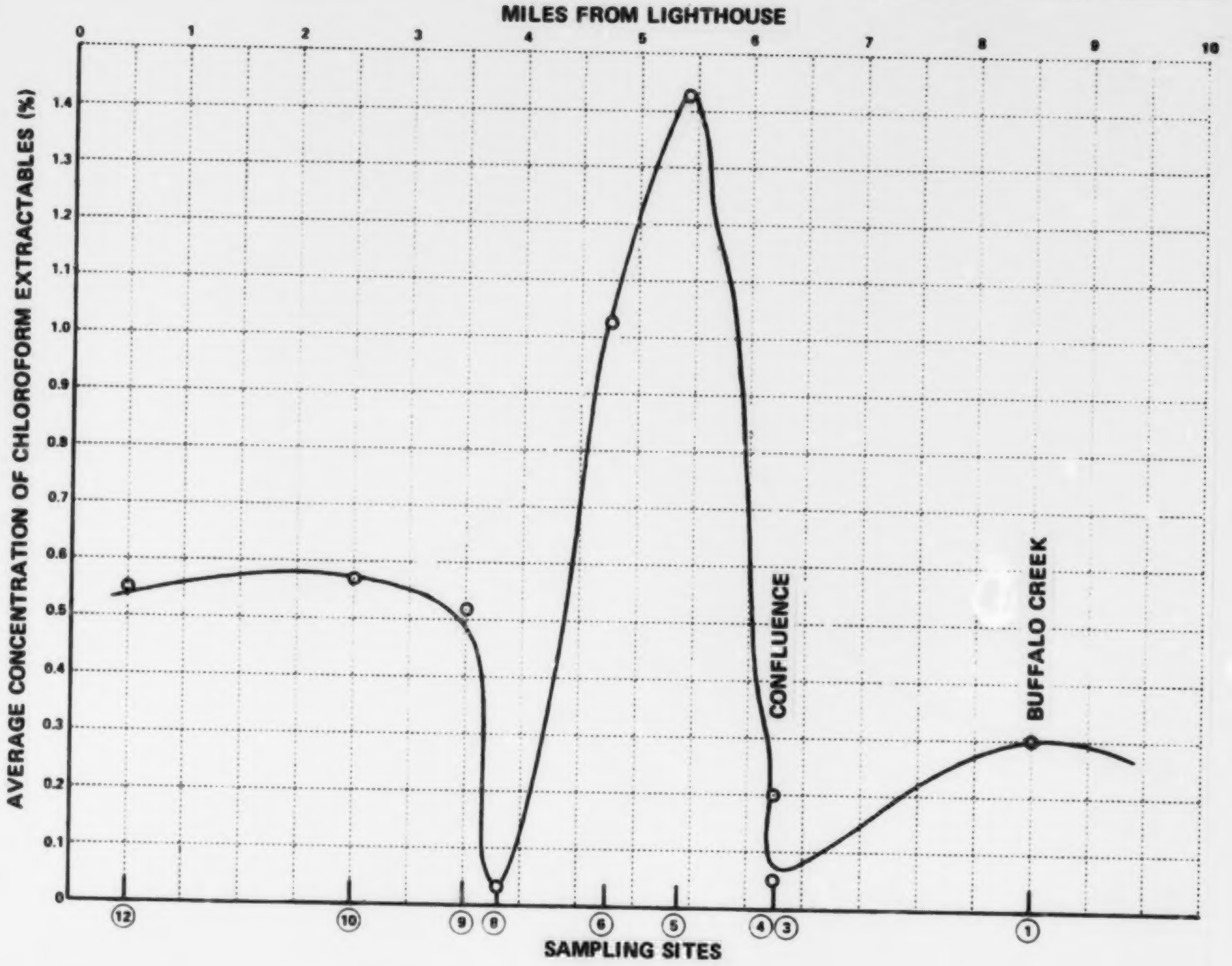


Figure 58 AVERAGE CHLOROFORM-EXTRACTABLE MATTER IN BUFFALO RIVER BOTTOM SEDIMENTS

demonstrates the intensification of bottom pollution in the highly industrialized sector. No estimate is yet available of the sedimentation rate in the Buffalo River itself, nor of the total amount of sediment already accumulated. In the absence of these data, it is not yet possible to compute the total burden of oily pollutants supported in the sediments of this industrial watercourse.

EVALUATION OF SHORELINE DEPOSITION OF OILY POLLUTANTS

During the late 1968 and early 1969 sampling programs, very large deposits of oil were noticed along the upper river shores as compared with small amounts of oil along the shorelines at the pneumatic barrier site near the Michigan Avenue Bridge and near the mouth of the Buffalo River at Lake Erie. These observations suggested that studies of the mechanisms of shoreline deposition of oil and the potential "sink" that the shoreline might represent for the pollutant oils in the River were worth pursuing. During the 1969 sampling season, the experimental plan was to allow the deposition and collection of the maximum amount of oil on test strips placed along the shoreline. Accordingly, to collect data on the transport of surface oils to the shoreline, ten aluminum strips coated with absorbent muslin cloth were attached to a large supporting panel as shown in Figure 59. Similar panels were then placed along the River at sampling points 2, 4, 5, 7, and at the Michigan Avenue Bridge (pneumatic barrier site) as shown in Figure 2.

Figure 60 is a photograph of a typical test panel in position at Site 5, the South Park Bridge Site. Each of the sampling boards was so placed that the individual sampling strips were approximately two-thirds submerged in the River water. Each week over a ten-week period a strip was removed and the total oil content collected on the muslin was determined by simple weighing. Over the course of the ten-week experiment, the muslin cloth deteriorated rapidly. Consequently, over the course of the ten-week experimental period, new muslin strips were installed from time to time and appropriate adjustments made in the oil accounting records.

During 1970, a five-week sampling program was undertaken to assess shoreline deposition in a simpler manner and with two different goals. The first goal was to simplify the field equipment sufficiently to suggest its general use in other industrial water watercourses. The second goal was to choose sampling surfaces so designed that the minimum, rather than the maximum, amount of oil would be collected. In order to meet these goals, base (no muslin cloth) aluminum strips were placed on the banks of the River at three different sampling sites, two of which reproduced sampling sites of the 1969 season, and one of which was located farther downstream in the granaries segment of the Buffalo River. In 1970, as in 1969 and 1968, it was evident that much greater quantities of oil were deposited along the banks in the upper river and industrial sections than farther downstream in the granary sector.

As illustrated schematically in Figure 61, each strip used for shoreline sampling during the 1970 sampling program consisted of two 3-foot-long sections of 4-inch wide aluminum flashing which were placed on top of one another and taped together along their outer edges with waterproof tape. Aluminum flashing was chosen because it is known to be available at building supply stores in most sections of the country. The taping

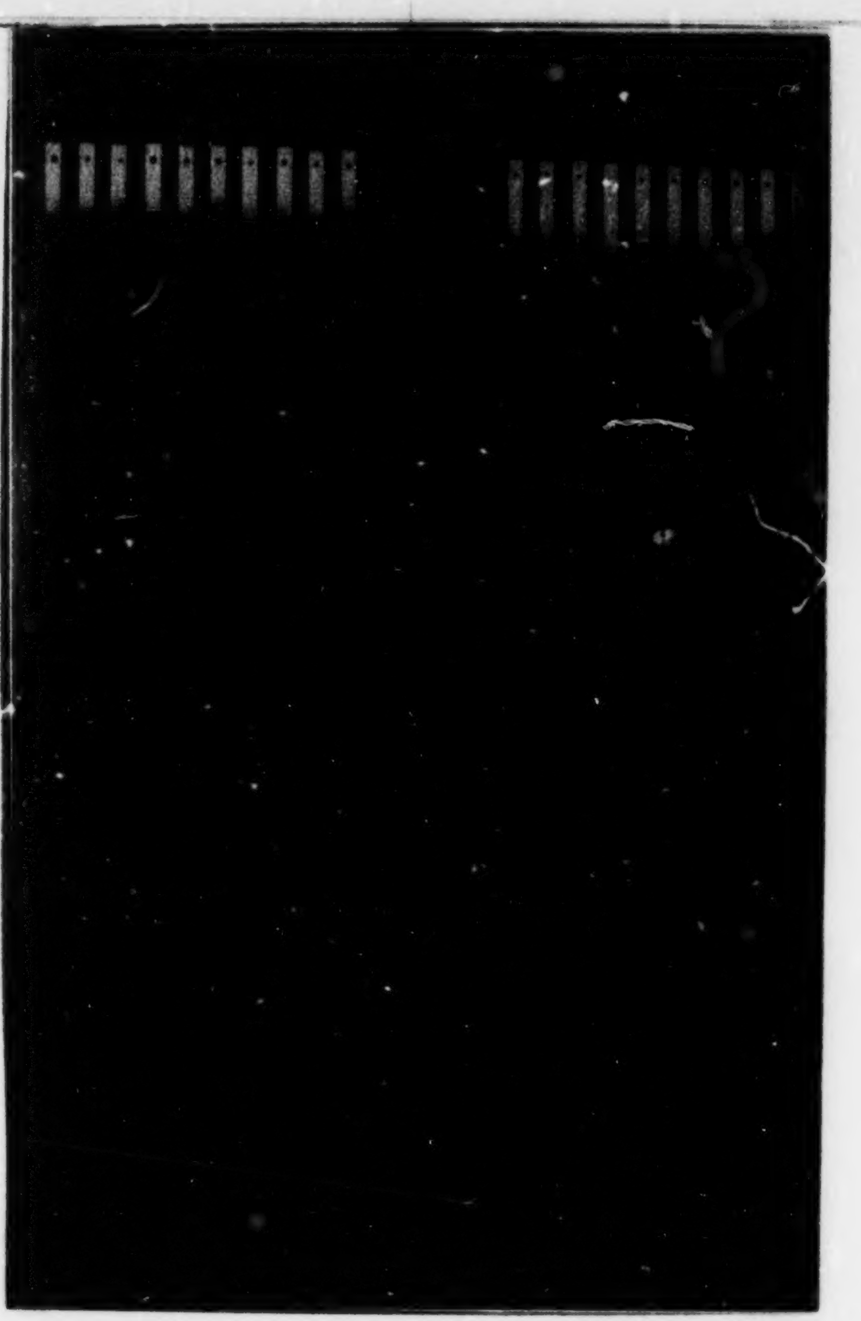


Figure 59 TEST PANELS USED TO ESTIMATE MAXIMUM AMOUNT OF SHORELINE-TRAPPED OIL

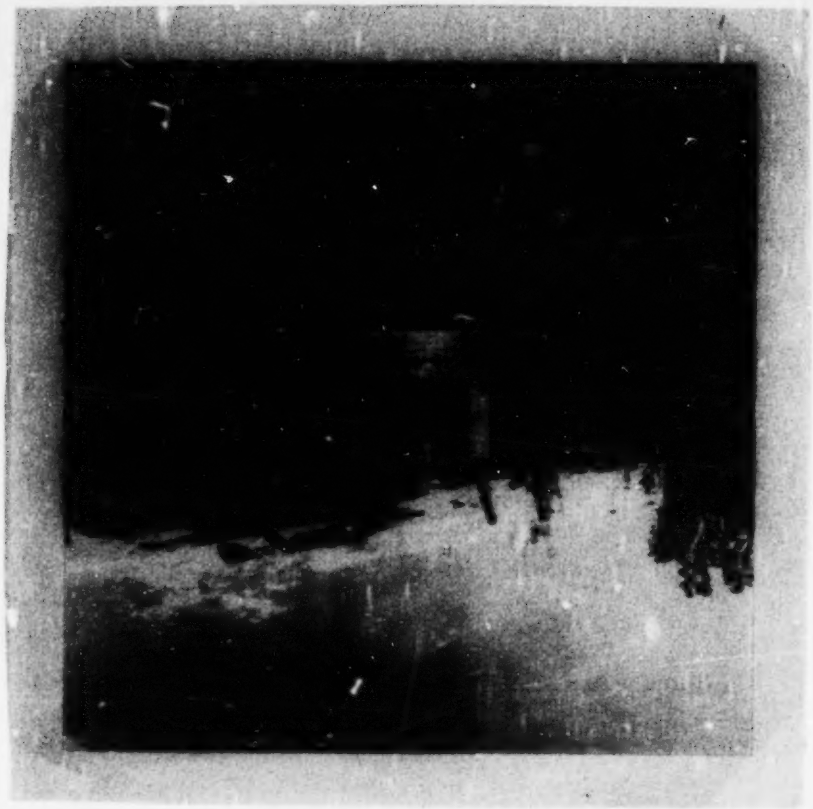


Figure 60 TEST PANEL IN POSITION AT SOUTH PARK BRIDGE SITE (SAMPLING SITE 5–FIGURE 2)

together of the two strips facilitated their ready separation and allowed the recovery of the strips with oil deposits only on the outer surface facing the water. By thus separating the two sections of aluminum flashing after the strip was removed from the bank, any deposits of oil trapped under the strip or attached to it from pollutant loads already present when the strips were placed could be discarded.

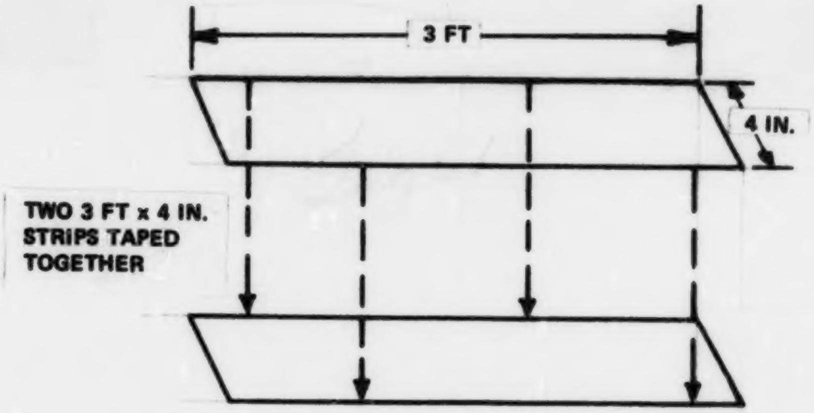


Figure 61 DISTORTED SCHEMATIC VIEW OF SAMPLING STRIPS FOR ESTIMATING MINIMUM AMOUNT OF SHORELINE-TRAPPED OIL

RESULTS

During the 1969 sampling season, when the maximum amounts of shoreline deposition were studied, the following results were obtained. Upstream of the greatest input of oily effluents from the major chemical industries (Site 2), it was noted that over the ten-week period, eight of the ten weeks saw additional amounts of the oil deposited along the shoreline, while two of the ten weeks saw net losses. The gross oil deposition over this period amounted to some 5,000 grams per square meter while the net losses were only about 10% of this, or about 500 grams per square meter. The net oily deposition at this location for the ten-week sampling period was approximately 450 grams per square meter per week or approximately 1 lb of oil per square meter per week.

Moving slightly downstream to sampling Site No. 4, over the same ten-week sampling period, net depositions were noted over seven separate weekly periods and net losses of oil back to the stream were noted over three weekly periods. The gross oil deposition amounted to about 1300 grams per square meter, and net loss was about 900 grams per square meter. Thus over the ten weeks, a net deposition rate of approximately 40 grams per square meter per week was observed.

At sampling site No. 5, directly across from many of the major outfalls of a large chemical plant, a net increase in the amount of oil deposited upon the shoreline was noted for seven weeks of the ten-week sampling period and a net loss from the shoreline back to the River surface was noted for the remaining weeks. The gross oil deposition over the ten-week period amounted to some 4600 grams per square meter and the net loss approximately 1300 grams per square meter for a net deposition rate of approximately 330 grams of oil per square meter per week at site No. 5.

For sample site No. 7, on the upwind side of the prevailing southwesterly winds and so far downstream that it was beyond the influence of the heavy chemical industries, it was noted that net losses over the sampling period occurred on only two of the weeks and that over the ten-week sampling period the average deposition was 42 grams of oily pollutants per square meter per week.

During the five-week verification program in 1970 when the sampling surfaces were changed to smooth aluminum strips, to collect only the minimum amount of oil possible, the following results were achieved:

1) At site No. 2, a net loss of oil was observed during only one week of the five-week sampling period and over the period the net deposition was approximately 17 grams per square meter per week.

2) At sampling site No. 7, a net loss to the River surface occurred on two dates over the same sampling period and the net deposition was less than one gram per square meter per week.

3) At sampling site No. 9 farther down river into the granary sector, there was no occasion when a loss from the shoreline to the stream was noted. Over the five-week period there was a net accumulation of approximately nine grams per square meter per week. This latter sampling point illustrates that a considerable amount of oil deposition can occur far downstream from the major sources even against the prevailing winds which tend to trap the surface oils in the upstream segment. However, as far downstream as the Michigan Avenue Bridge, no significant quantities of oil were observed to be deposited upon the shoreline in either 1969 or 1970.

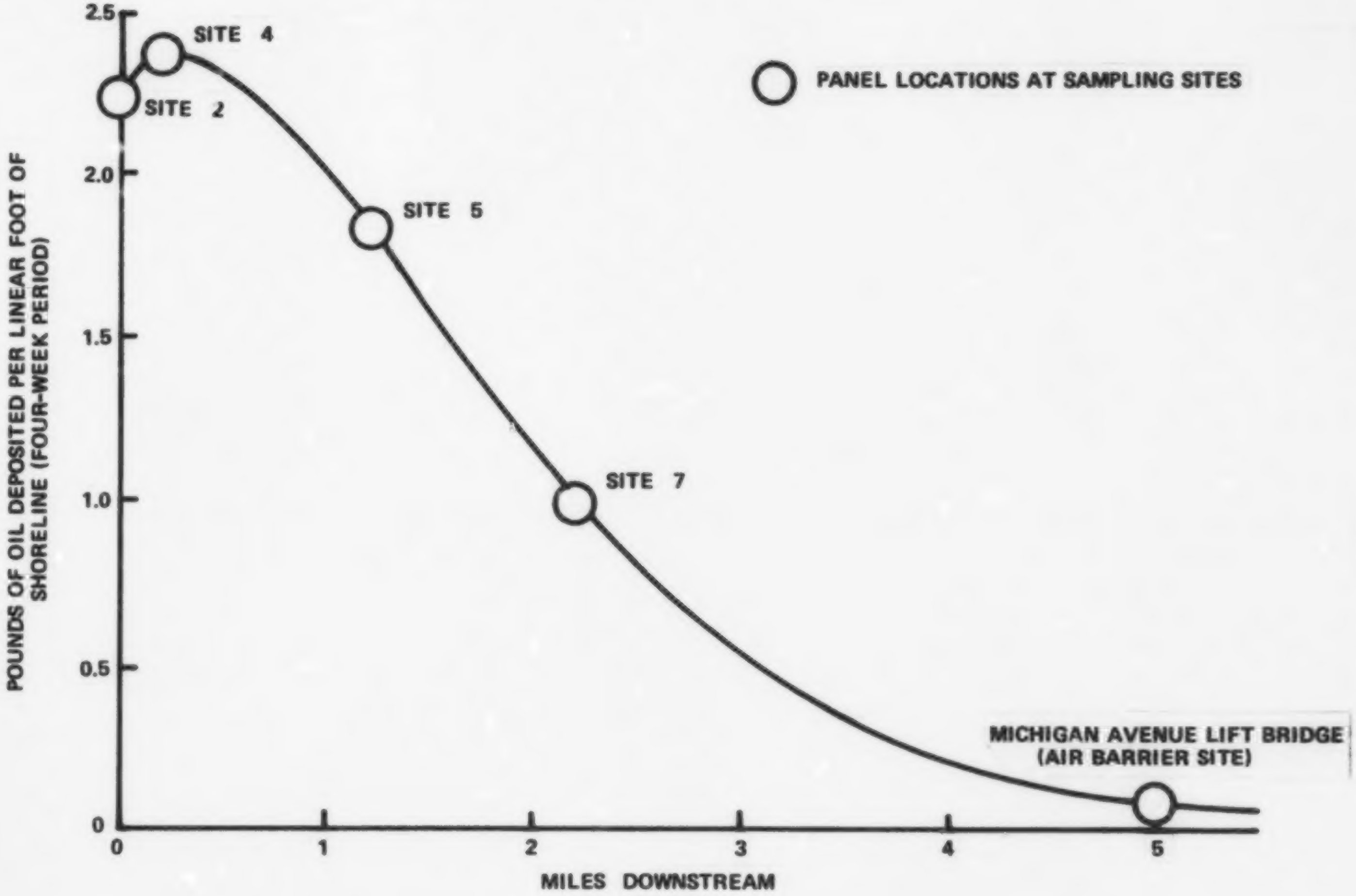
Thus, the results of the 1969 and 1970 shoreline sampling programs provided quantitative confirmation of the visual impression that shoreline deposition is a continuous sink for some of the pollutant oils in the Buffalo River. As one moves from the upstream industrialized section to the downstream granary section, the oil accumulation along the shoreline decreases significantly. In fact, on given days, deposition in the upper River segment was measured to be as much as 100 times greater than at the Michigan Avenue Bridge. The data showed that loss of oil from the shoreline does occur, although much less frequently and certainly in smaller quantities than the transfer of oil from the water to the shoreline.

Variations in oil concentration along the shoreline in the upper River are illustrated by the simplified plot of Figure 62. This plot of oil deposition per foot of shoreline illustrates that a natural surface barrier can be formed by the physical features of the River. The barrier is composed of the zig-zag curves and turns of the River and is assisted by the reverse flow caused by rising of the Lake level and by the predominant upriver wind. It should be noted that the plot given in Figure 62 is illustrative of only one particular four-week period and does not necessarily match the situation over any other given four-week period or over a very long time span. However, taking the values typical of the upper River segment, it can be estimated that between 1000 and 4000 lb of oil per day are potentially deposited along the shoreline in the approximately two-mile length of the industrialized area. The range of this estimate takes into account the variations known to exist in the shoreline slope and the unequal concentrating effects of the wind along the opposite sides of the River.

DISCUSSION OF RESULTS

In both the 1969 and 1970 shoreline sampling programs, it became evident that significantly greater amounts of oil were deposited along the boundaries of the upper River section than were deposited in the lower River segments. Periods of oil loss from the shores in some sections with overall net increases were also noted. In an attempt to establish a relationship between flow of the Buffalo River and the amount of oil deposited on the shore, data from both the 1969 and 1970 shore sampling programs were examined in conjunction with the reported discharge from the Buffalo River tributaries. It was conjectured that at low tributary discharges, shoreline deposition would be high and that at higher discharges, the oily sludge deposits might be eroded from the banks. However, examination of the mean daily discharges occurring between sampling periods revealed that oil deposition occurred to at least as great an extent, and in some cases to a greater extent, during periods of high flow from the tributaries as during periods of low flow. The periods of sludge removal from the banks might thus be best associated with sudden increases in discharge from the relatively low flows (less than 60 cu ft/sec combined discharge of the tributaries) rather than during extended periods of high flow rates. Yet an exception to this suggestion is noted over the one-week period from August 28 to September 4, 1969, when oil losses occurred during a period of uniformly low flow. A complication in this observation is that the occurrence of the Labor Day weekend during this weekly period and the noted accompanying lower level of industrial activity might have also been influential.

A further interesting observation was that on September 18 and September 30 of 1970, greater than average concentrations of oil were measured in the bulk water and the surface water samples. These greater-than-average concentrations of oil suspended within the Buffalo River bulk water phase itself coincided with losses of oil from the shoreline strips along the banks. This indicates that perhaps more oil is available for skimming on days that erosion of oily sludge from the banks has occurred.



(NOTE: OTHER PATTERNS OF DEPOSITION WERE NOTED OVER DIFFERENT PERIODS)

Figure 62 PLOT OF SHORELINE DEPOSITION OF "OILY" POLLUTANTS ALONG THE BUFFALO RIVER AS ACCUMULATED OVER A SINGLE 4-WEEK PERIOD

A further interesting observation was the occurrence of abundant growths of algae on silt-laden strips placed in the granary sector, whereas strips placed farther upstream, which were coated with typical amounts of oily sludge, contained much less algae. Nevertheless, appreciable amounts of algae were found attached to the oily sludge deposits all along the Buffalo River banks. Dr. Robert Sweeney of the Great Lakes Laboratory, State University College of New York at Buffalo has identified these algae as a strain of filamentous Cladophora.

Superimposed on all these variations in the shoreline deposition rate was a variability in the chemical character of the shoreline deposits. Figure 63 shows, for example, infrared spectra which illustrate changes in the chemical character of a shoreline oil deposit at two different sites over a single week period. The top two traces in Figure 63 illustrate changes in the character of the shoreline deposits at site 2 over a one-week period. It is interesting to note that over this period there was a net increase of some 73 grams per square meter of oily pollutants deposited along the strips and yet the infrared spectra show that there had been a net decrease in the kinds of organic pollutants present. Two possible explanations are: (1) that the oil was completely changed in character over the one week period by a process of net loss and net deposition, or (2) that the oil originally present was mixed with some biological material which was eliminated during the course of the addition of the extra oil.

The bottom two traces in Figure 63 are for site 7. This site also experienced a net increase (some 28 grams per square meter) of oil for the same one-week period considered for site 2. In the present case, the infrared spectra show a change in character of the oil indicating a greater degree of oxidation associated with its weathering as evidenced by the enhancement of the ester band at about 1720 cm^{-1}.

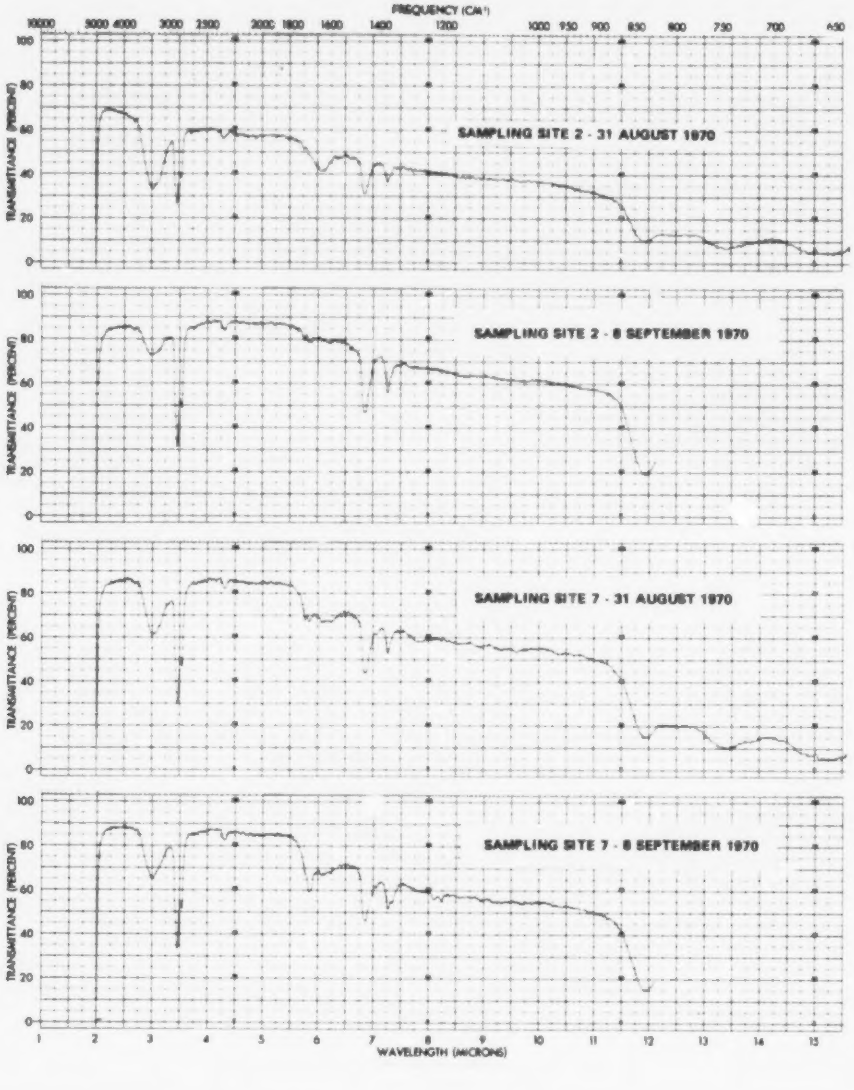


Figure 63 INFRARED SPECTRA SHOWING CHANGES IN THE CHEMICAL CHARACTER OF THE SHORELINE OIL DEPOSITS OVER A SINGLE WEEK

CHARACTERIZATION OF INDUSTRIAL OUTFALLS AND THEIR CORRELATION WITH POLLUTANT FILMS FOUND AT THE RIVER SURFACE

INTRODUCTION

Throughout this work, in order to secure a reliable sample of an industrial outfall or effluent overflow, care was taken to locate a point of free fall where the sample collector could be passed at a uniform speed through the entire stream. As a result of our regular field sampling program during 1969 and 1970, we obtained a comprehensive view of the industrial pollutants being discharged into the Buffalo River and of the obvious oily slicks which consequently accumulate over the River surface and mark it as a grossly polluted stream, indeed at times a fire hazard.

Figure 64 is a composite infrared spectrum of all the pollutants now recognized as being regularly discharged into the industrial watercourse from the major industries along the River. This artificial spectrum was created by superimposing the typical traces from each of the major industrial sources, examples of which are shown in Figures 67 and 68. The major infrared absorption band centered at 2900 cm^{-1} noted in each of these spectra is associated with the presence of oils or oil-based organic pollutants as are two less intense bands which bracket the 1400 cm^{-1} frequency line. The rest of the complexity in the composite spectrum in Figure 64 can be attributed almost completely to the presence of the large variety of dyes present in effluents from the General Chemical Division of the Allied Chemical and Dye Corporation which is referenced throughout this report by its earlier name, the National Aniline Corporation. The composite spectrum of Figure 64 also includes absorption bands characterizing some proteinaceous effluents from the various sewer overflows and from the granaries along the lower half of the River.

If the obvious surface pollution of the Buffalo River is predominantly of industrial origin, no spectrum characterizing a "natural" midstream pollutant slick should be substantially more complex than the artificial summation spectrum given as Figure 64. Neither should such a spectrum include absorption peaks not present in Figure 64. Actually spectra simpler than the composite are almost more certain to be found because of the already noted lack of opportunity for thorough mixing of the various pollutants on the River surface from the geographically separated sites along the River.

Figures 65 and 66 represent compilations of "natural" film infrared spectra taken during the 1969 and 1970 sampling seasons. With the exception of two spectral bands indicated by arrows in the first and sixth traces of Figure 65 all these diagnostic infrared absorption regions are easily accounted for by the known industrial pollutants whose spectra are highlighted in Figures 67 and 68. The two bands not

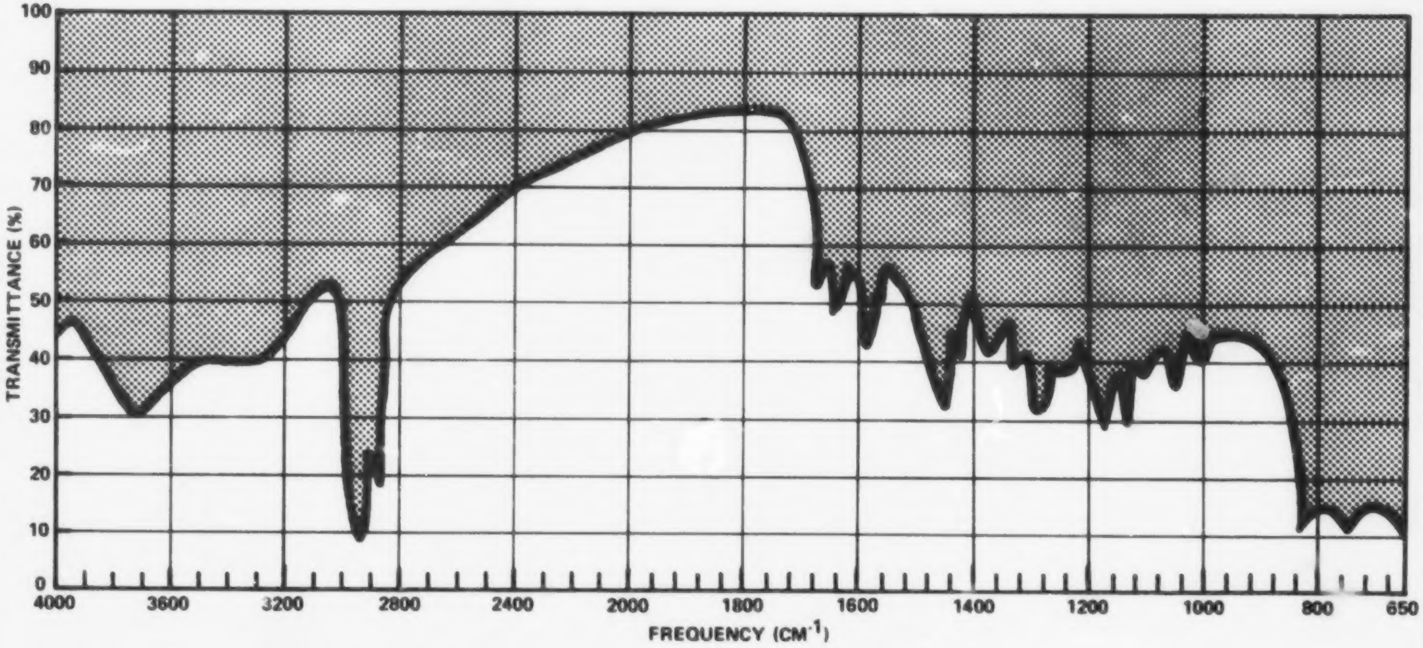


Figure 64 COMPOSITE INFRARED SPECTRUM OF MAJOR BUFFALO RIVER POLLUTANTS DERIVED FROM INDUSTRIAL OUTFALLS

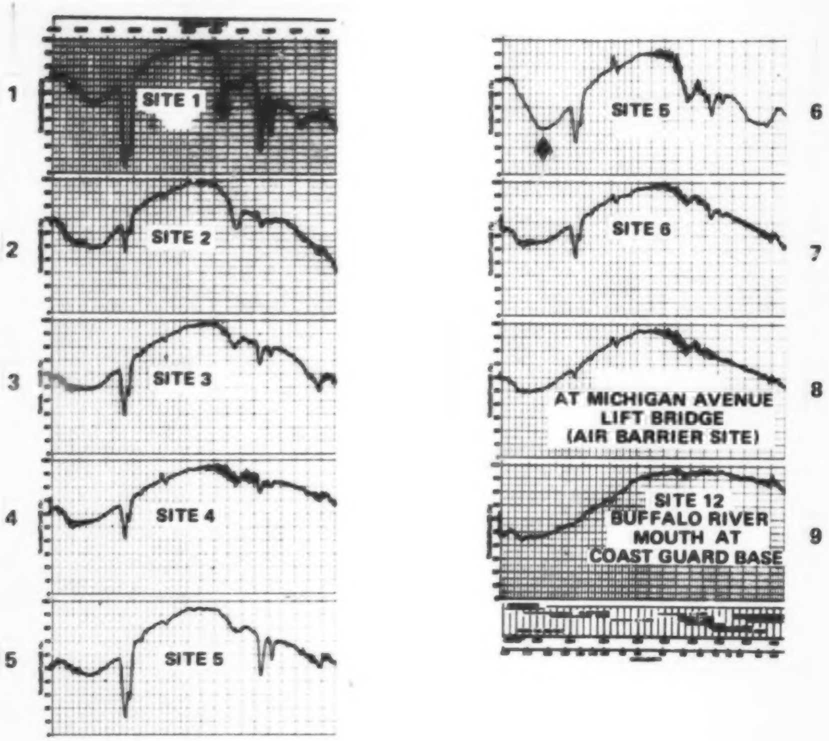


Figure 65 CHARACTERISTIC INFRARED SPECTRA OF POLLUTANT FILMS AT MIDSTREAM SURFACE LOCATIONS IN BUFFALO RIVER (ARRANGED IN SEQUENCE --1 THROUGH 9-- FROM UPPER RIVER TOWARDS MOUTH) DURING 1969 SAMPLING PROGRAM

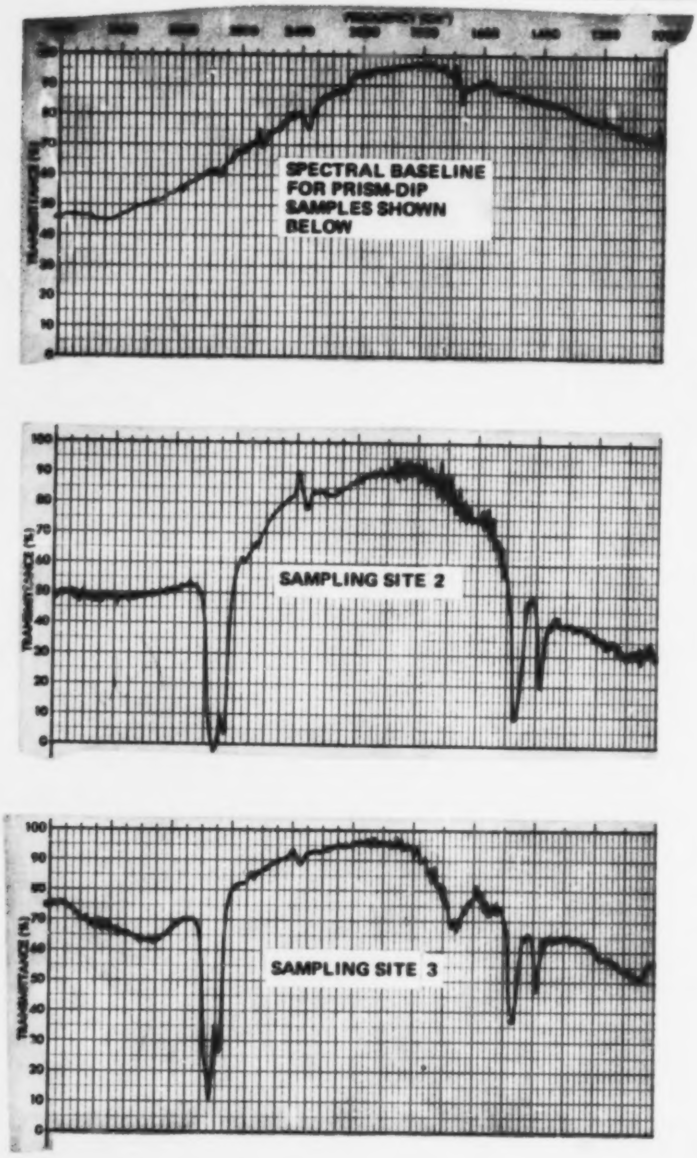


Figure 66 CHARACTERISTIC INFRARED SPECTRA OF POLLUTANT FILMS AT MIDSTREAM SURFACE LOCATIONS IN BUFFALO RIVER (ARRANGED FROM TOP TO BOTTOM IN SEQUENCE FROM THE UPPER RIVER TO MOUTH) DURING 1970 SAMPLING PROGRAM (SHEET 1 OF 3)

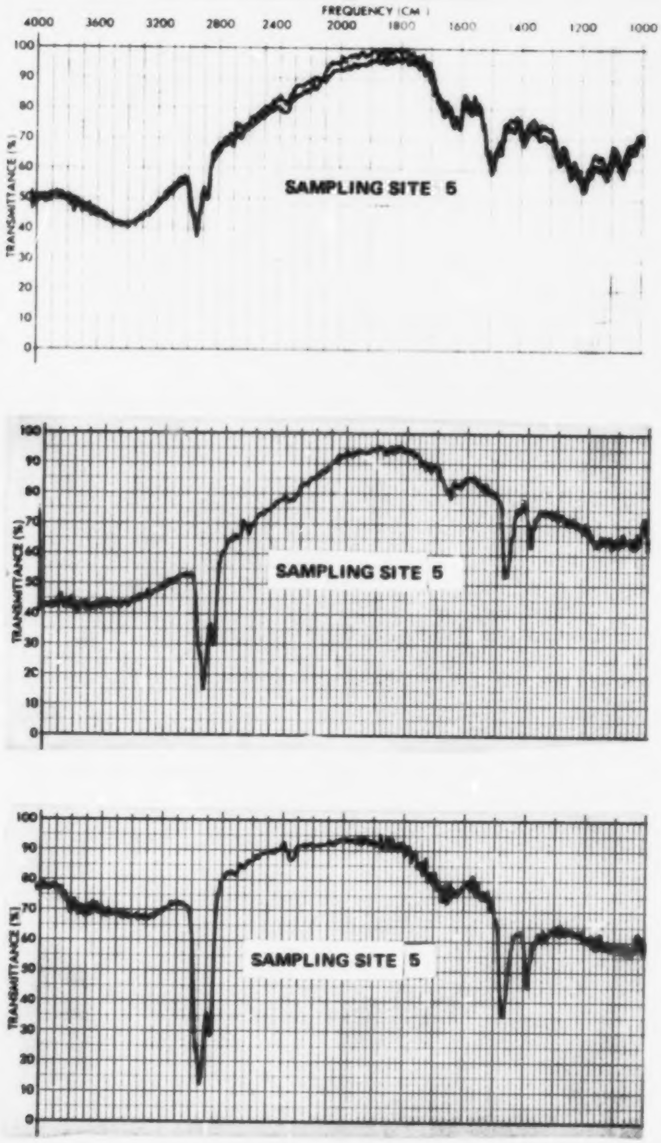


Figure 66 CHARACTERISTIC INFRARED SPECTRA OF POLLUTANT FILMS AT MIDSTREAM SURFACE LOCATIONS IN BUFFALO RIVER (ARRANGED FROM TOP TO BOTTOM IN SEQUENCE FROM THE UPPER RIVER TO MOUTH) DURING 1970 SAMPLING PROGRAM (SHEET 2 OF 3)

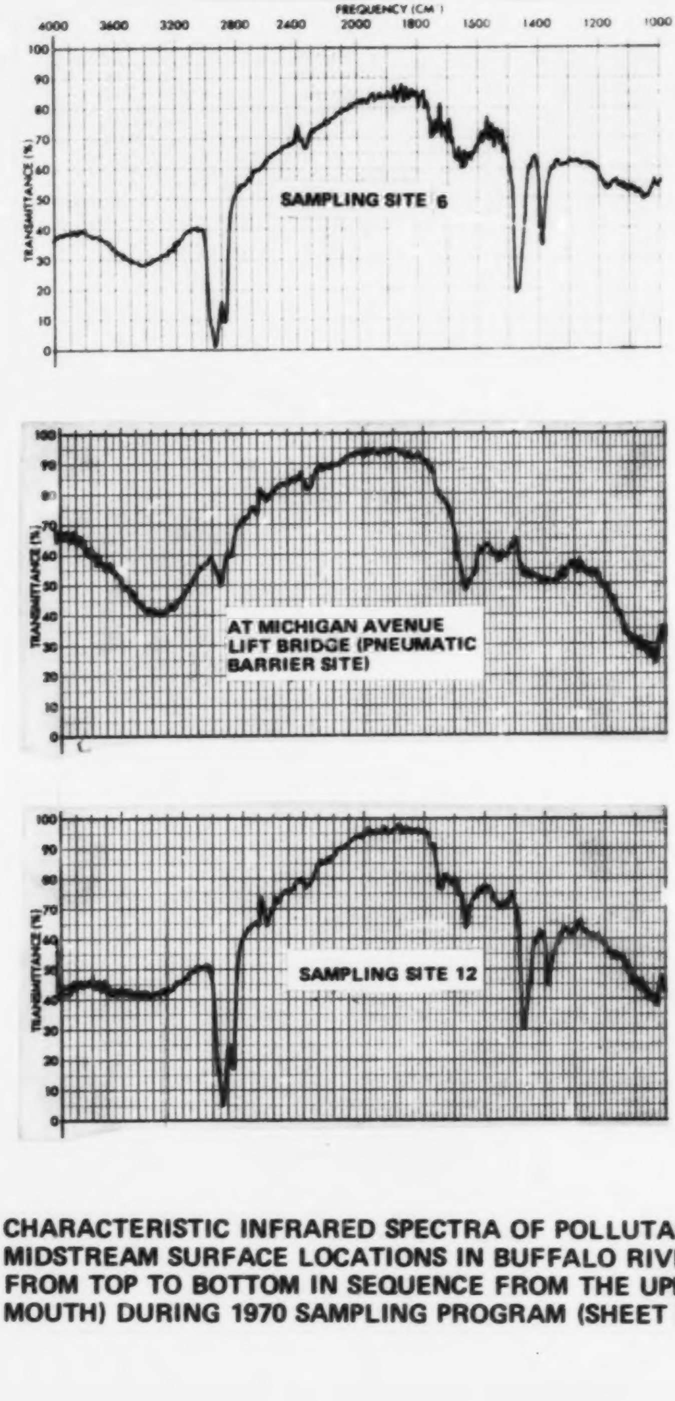


Figure 66 CHARACTERISTIC INFRARED SPECTRA OF POLLUTANT FILMS AT MIDSTREAM SURFACE LOCATIONS IN BUFFALO RIVER (ARRANGED FROM TOP TO BOTTOM IN SEQUENCE FROM THE UPPER RIVER TO MOUTH) DURING 1970 SAMPLING PROGRAM (SHEET 3 OF 3)

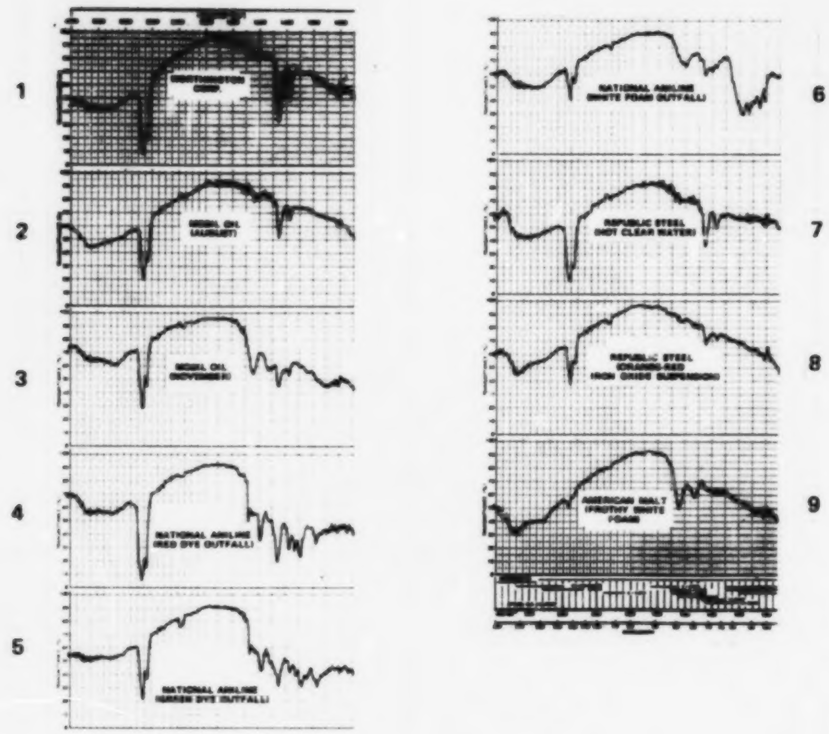
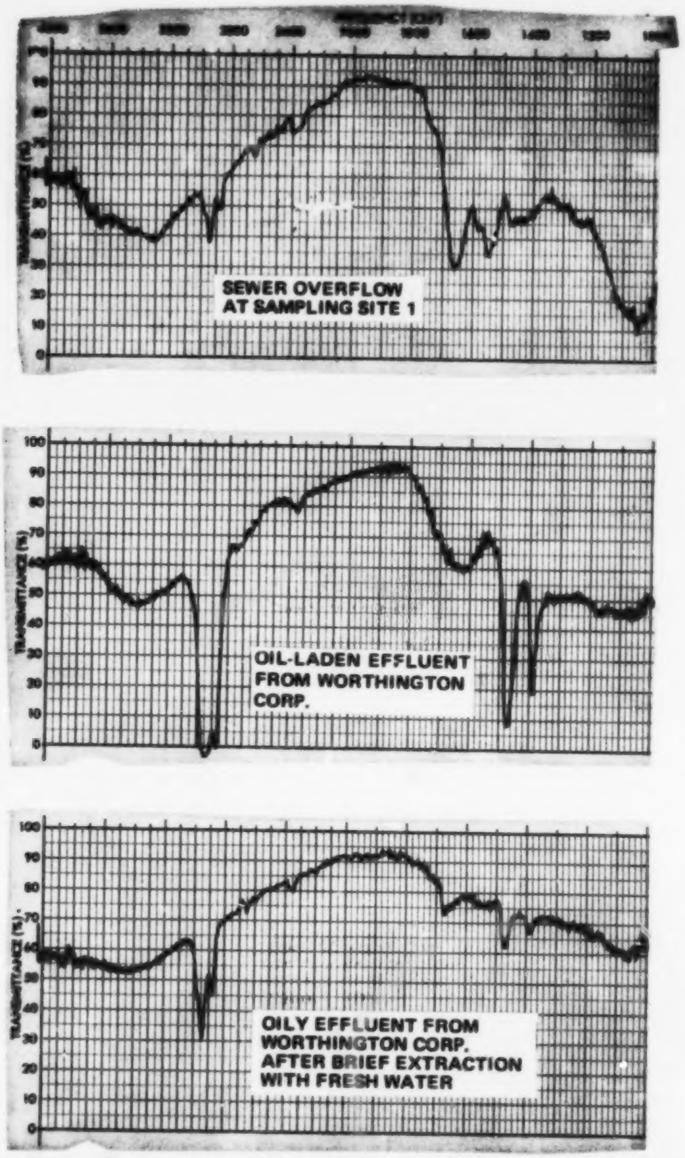


Figure 67 **CHARACTERISTIC INFRARED SPECTRA OF POLLUTANTS DISCHARGED IN VARIOUS INDUSTRIAL OUTFALLS ALONG THE BUFFALO RIVER (ARRANGED IN SEQUENCE --1 THROUGH 9-- FROM UPPER RIVER TOWARDS MOUTH) DURING 1969 SAMPLING SEASON**



NOTE: PHOTOGRAPHS OF THESE SPECIMENS APPEAR IN THIS SAME SEQUENCE IN FIGURE 69.

Figure 68 INFRARED SPECTRA OF DRIED RESIDUES FROM OUTFALL SAMPLES COLLECTED (ON SAME DAY) IN SEQUENCE FROM UPPER BUFFALO RIVER TO LAST MAJOR INDUSTRY DOWNSTREAM (SHEET 1 OF 3)

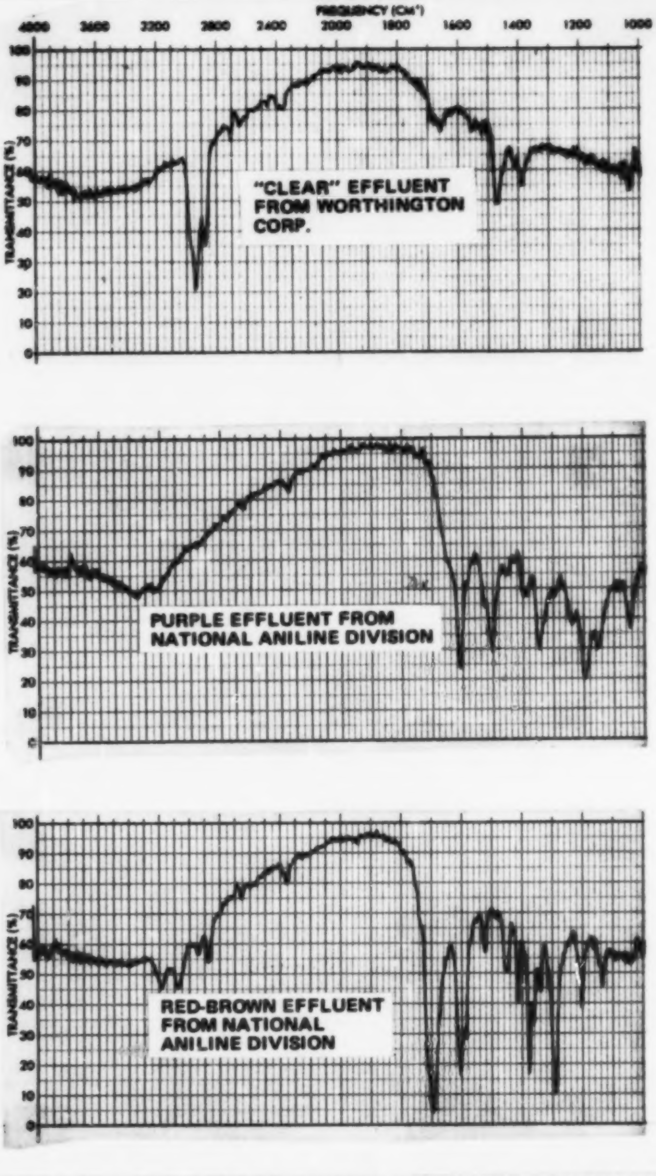


Figure 68 INFRARED SPECTRA OF DRIED RESIDUES FROM OUTFALL SAMPLES COLLECTED (ON SAME DAY) IN SEQUENCE FROM UPPER BUFFALO RIVER TO LAST MAJOR INDUSTRY DOWNSTREAM (SHEET 2 OF 3)

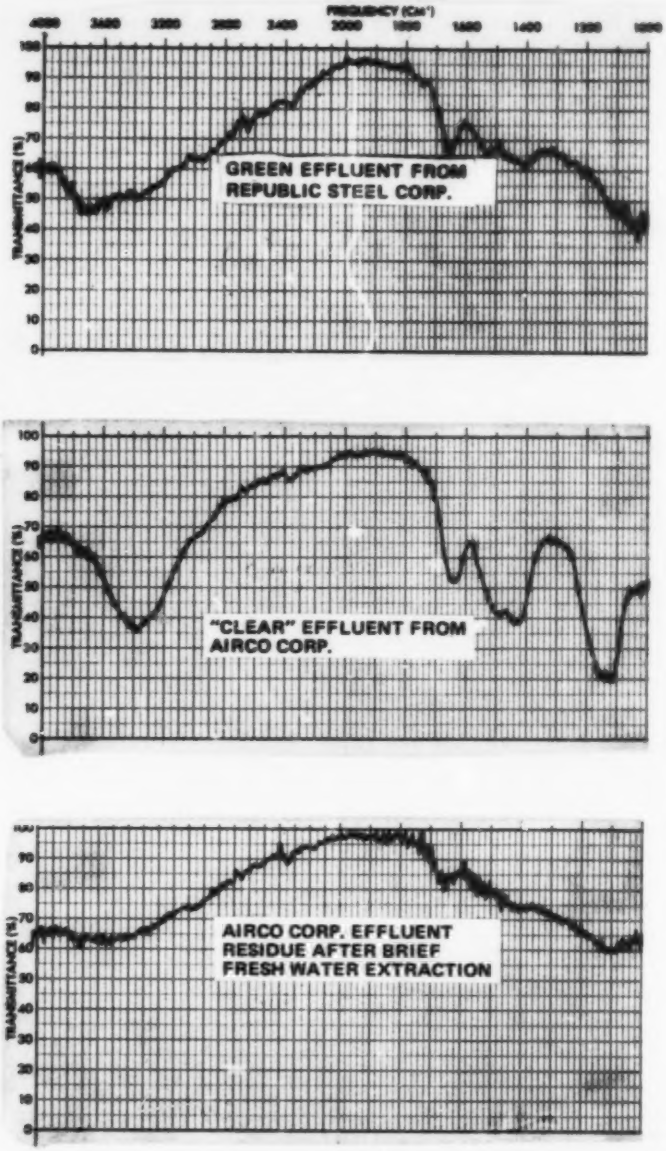


Figure 68 INFRARED SPECTRA OF DRIED RESIDUES FROM OUTFALL SAMPLES COLLECTED (ON SAME DAY) IN SEQUENCE FROM UPPER BUFFALO RIVER TO LAST MAJOR INDUSTRY DOWNSTREAM (SHEET 3 OF 3)

accounted for by industry are typical of biological products which are known to be entering the River in large quantities from the various sewer overflows and from the municipalities farther upstream than considered during the course of this Buffalo River project. It is appropriate to examine closely the diagnostic infrared spectra collected in Figures 65 through 68. Note that these figures contain infrared traces arranged in sequence from the upper River reaches to the lower River reaches terminating in most cases at the juncture of the Buffalo River and Lake Erie (labelled as Site 12 in the overview of the sampling sites provided in Figure 2). Altogether these figures vividly represent a major feature of the Buffalo River. That is, almost all of the oil pollution sources are in the upper River and most of the surface oil remains in the upper River segments. In addition to trapping of the discharged oil in the very obvious oil slicks characterized here, it should be recalled that a large amount of the oil is also trapped along the shoreline by the natural barriers provided there, and entrapped in the bottom sediments, as discussed earlier.

Figures 67 and 68, for example, characterize the copious, almost pure hydrocarbon components derived from the Worthington Corporation, from the Mobil Oil Refinery and from the Republic Steel Corporation, all in the upper River shorelines, during the 1969 and 1970 sampling periods. The qualitative properties of the oils discharged vary among these industries with the Worthington outfall having the character of a light cutting oil, the Mobil Oil Refinery discharging predominantly mixed refinery tailings incorporating a large portion of low-chain-length petroleum distillates, and the Republic Steel Plant adding high molecular weight, tarry residues (often in a hot water discharge) which condense into thick black puddles upon cooling at the Buffalo River surface. A substantial amount of oil is also discharged in the brightly colored and sometimes very foamy dye effluents from the National Aniline Plant and in an iron oxide loaded stream from Republic Steel Corporation. As one proceeds downriver from these industries, the major pollution sources dramatically change from oil-laden effluents to protein-laden effluents as the major shoreline industries change from oil and chemical plants to granaries and cereal producers. The last major easily identified industrial outfall along the River is that of the American Malt Company which is still a long distance upstream and many turns from the River mouth. The common effluent from the American Malt outfall produces a frothy white foam which analysis shows to be an almost pure protein. Copious amounts of this potential biological nutrient are discharged along this section of the River, but seem not to contribute to the obvious surface pollution by oils. On the other hand, this severe enrichment of the watercourse in biodegradable material when coupled with the equally rich discharges of proteinaceous matter from sewer overflows should be taken into account when considering the overall stream quality of the Buffalo River.

Cross comparison of the infrared spectra collected in Figures 65 through 68 will illustrate that the midstream pollutant slicks are often readily associated with near-by industrial outfalls giving rise to them. For instance, the spectra of the surface films in the industrial segments of the River often contain infrared bands that can only be correlated with the colored dyes in the effluents from the National Aniline Corporation.

In the 1969 sampling season, it was found that there was uniform absence of surface oil slicks or surface oil outflow at the Buffalo River mouth. On the other hand, during the 1970 sampling season there were quite often obviously thick and apparent oil slicks over the entire length of the Buffalo River, including its mouth at Lake Erie.

The outfall samples collected and characterized by their infrared spectra in Figure 68 were selected from a series collected in the River all on the same day. They include specimens of major outfalls from both the upper River and the lower River segments. Photographs of test-tube quantities of these same specimens appear in Figure 69 in the same sequence as presented in Figure 68.

In Figure 69, the outfall samples are arranged in sequence from the uppermost river portions to the last major industry downstream. From left to right in the photo these contributions to the River are as follows: (1) a sewer overflow at Sampling Site 1, (2) an oil-laden effluent from the Worthington Corporation (note in the photograph the very thick layer of congealed oil collected at the surface of this particular tube), (3) an apparently clear effluent from the Worthington Corporation whose infrared analysis showed it to contain an abundant amount of emulsified oil, (4) a purple effluent from the National Aniline Corporation, followed by (5) a very bright red-brown effluent from National Aniline, (6) a green effluent from the Republic Steel Corporation which despite its very bright color did not contain a large amount of solubilized oil on that particular sample day, (7) a clear effluent from the Airco Corporation which, although it contained a large quantity of dissolved salts, did not contain much oil. The second last sample (8) shown in Figure 69 is a specimen from a sewer overflow from Site 7 in the Buffalo River. Sample (9) was of surface water near the Michigan Avenue Bridge (the air barrier site). The final capped test tube illustrated in the photograph (10) is the distilled water used as an analytical control during chemical work-up of these samples. The infrared spectra of most of these samples are presented in Figure 68, and spectra of some of the surface water beneath the oil slicks at these same locations are presented in Figure 70.

Figure 70 shows typical infrared spectra of residues from simple evaporation of Buffalo River surface samples collected on one day in a sequence from the upper River to the mouth at Lake Erie. The subsurface water at Site 3 contained a large quantity of both protein and polysaccharide-type compounds, most likely from sewage effluents upstream. At Site 5, these components were slightly degraded but not strikingly supplemented by oils or dyes in the subsurface water. At the Michigan Avenue Bridge, the infrared spectrum of the residues (from evaporation of an aliquot of the subsurface water there) showed a very

1 SEWER OVERFLOW AT SAMPLING SITE 1
2 OIL-LADEN EFFLUENT FROM WORTHINGTON CORPORATION
3 APPARENTLY "CLEAR" EFFLUENT FROM WORTHINGTON CORPORATION
4 PURPLE EFFLUENT FROM NATIONAL ANILINE DIVISION
5 RED-BROWN EFFLUENT FROM NATIONAL ANILINE DIVISION
6 GREEN EFFLUENT FROM REPUBLIC STEEL CORPORATION
7 "CLEAR" EFFLUENT FROM AIRCO CORPORATION
8 SEWER OVERFLOW AT SAMPLING SITE 7
9 SURFACE WATER AT PNEUMATIC BARRIER (NEAR MICHIGAN AVE. LIFT BRIDGE)
10 DISTILLED WATER (IN PLASTIC CONTAINER) FOR ANALYTICAL CONTROL

NOTE

INFRARED SPECTRA OF ALL SPECIMENS EXCEPT 8 AND 10 ARE GIVEN IN FIGURES 68 AND 70

Figure 69 OUTFALL SAMPLES COLLECTED (ON SAME DAY) IN SEQUENCE FROM UPPER BUFFALO RIVER TO LAST MAJOR INDUSTRY DOWNSTREAM

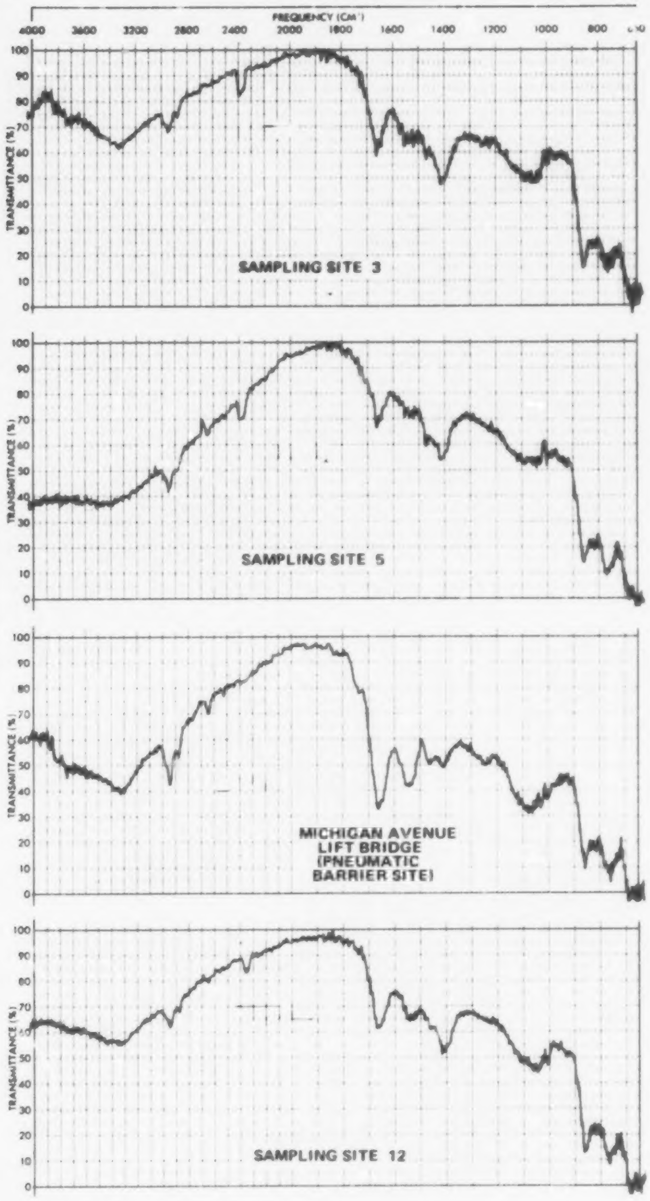


Figure 70 INFRARED SPECTRA OF RESIDUES FROM EVAPORATION OF BUFFALO RIVER SURFACE WATER SAMPLES COLLECTED (ON SAME DAY) IN SEQUENCE FROM UPPER RIVER TO MOUTH AT LAKE ERIE

pure biological spectrum suggesting the presence of a large amount of protein- and polysaccharide-type materials. This reflects the quality of inputs from the granaries and other cereal processors at that site. The final trace in Figure 70 once again shows a spectrum typical of predominantly biological material and not of large amounts of dissolved or suspended oil. It should be emphasized, however, that these spectra have been obtained from simple dried residues of the surface waters at these various locations. The contributions of oils from the industrial sources are much better illustrated in other spectra included in this section for the solvent extracts of the oil suspended in these waters.

MULTIPLE PARAMETER ANALYSIS OF INDUSTRIAL OUTFALL SAMPLES

Approximately 50 samples of industrial outfalls were collected in sufficient quantity that they could be characterized as to their pH, color, ultraviolet and infrared spectra, percent dissolved solids, and solvent extractable matter. Depending upon the pH of the samples, the solvent used for extraction was either chloroform (for samples of pH less than 8) or carbon tetrachloride (for samples of pH greater than 8). Table 16 lists some of the characteristics of chemical plant outfalls for samples collected over the 1970 sampling season. Note the extremely wide variation in pH in these samples, a very important parameter in judging the relative amount of control exercised by an industry on the character of its effluent. Note also that the dissolved solids content in these effluents ranges from less than one percent to over 20 percent in one extreme instance, although it is also noted that most of the outfalls did not even approach 1% dissolved solids over the 1970 sampling season.

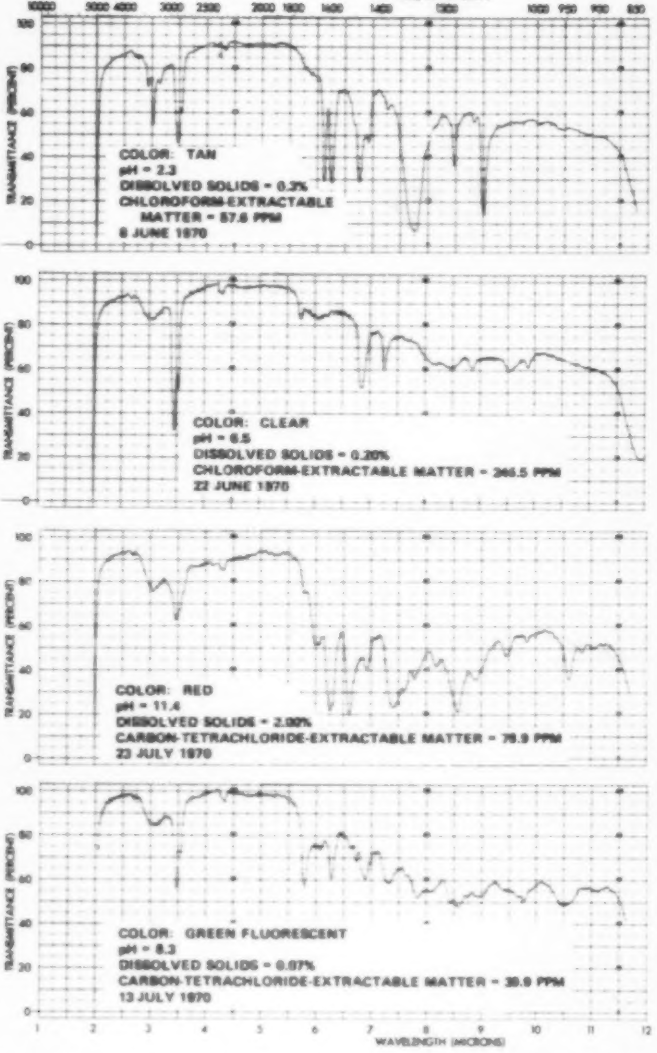
The outfall having the high percentage of dissolved solids is deserving of special attention for other reasons: (1) its density was 1.11 grams per cc, a substantial deviation from unity; (2) acetone, usually miscible in all proportions in water, was only 60% soluble in this industrial effluent on an equal volume basis; and (3) on heating and acidification of this sample, whose original pH was 8.4, an odor reminiscent of hydrogen sulfide emanated. Figure 71 is a collection of infrared spectra characterizing the solvent-extractable, oily pollutants in these extremely variable outfall samples collected from one major chemical plant on the Buffalo River over a two-month period (June and July 1970). Each spectrum is annotated with (1) the outfall color, (2) the outfall pH, (3) percent of dissolved solids, (4) the quantity of "oils" extractable with chlorinated solvents, and (5) the sampling date. It is to be noted that no two spectra in this figure are the same, illustrating the substantial variability in pollutants present in the discharges of this particular industry and the difficulty in interpreting the sampling results.

The second trace from the top in Figure 71 (Sheet 1) deserves special discussion. In this case the effluent was clear; it was only slightly acidic (pH = 6.5), and the amount of dissolved solids was only 0.2 percent. By all commonly used criteria, this would be considered an

Table 16

CHARACTERIZATION OF HIGHLY VARIABLE CHEMICAL PLANT OUTFALLS

DATE (1970)	COLOR	pH	% DISSOLVED SOLIDS	EXTRACTABLES (PPM)	
				CHLORO-FORM	CARBON TETRA-CHLORIDE
20 APRIL	BLUE-GREEN	9.1			3.0
20 APRIL	YELLOW (PEARL)	8.4	22.2		39.5
20 APRIL	RED	3.9		5.0	
18 MAY	YELLOW	11.8	0.382		65.4
18 MAY	TAN	5.3	0.056	73.3	
25 MAY	YELLOW	11.2	0.254		71.2
8 JUNE	TAN	2.3	0.304	57.6	
8 JUNE	RED	2.9	0.168	32.9	
8 JUNE	YELLOW	11.4	0.216		19.2
15 JUNE	YELLOW	3.5	0.112	25.6	
15 JUNE	GREEN	8.7	0.066		22.3
15 JUNE	YELLOW	12.1	0.487		50.6
22 JUNE	YELLOW	12.0	0.492		38.2
22 JUNE	GREEN	2.0	0.177	25.3	
22 JUNE	RED	3.9	0.175	35.0	
22 JUNE	WATER WHITE	6.5	0.204	246.5	
22 JUNE	BLUE	7.7	0.156		
29 JUNE	WATER WHITE	7.6	0.041	23.0	
6 JULY	LIGHT TAN	11.9	0.276		47.6
6 JULY	PINK	12.1	0.278		31.6
13 JULY	GREEN FLUORESCENT	8.3	0.065		39.9
13 JULY	RED	11.4	2.002		78.9
13 JULY	LIGHT GREEN FLUORESCENT	7.8	0.076	44.7	
13 JULY	PINK	7.9	0.043	21.3	
13 JULY	WATER WHITE	7.5	0.077	25.3	
21 JULY	TAN (#2)	8.7	0.128		28.5
21 JULY	ORANGE (#1)	8.6	0.068		50.0
28 JULY	WATER WHITE	9.2	0.148		10.0
28 JULY	WATER WHITE	10.0	0.144		15.3
28 JULY	DARK GREEN	7.5	0.590	39.0	
11 AUGUST	WATER WHITE (b)	7.5	0.089	23.8	
11 AUGUST	WATER WHITE (a)	7.7	0.042	25.0	
11 AUGUST	WATER WHITE	5.4	0.060	18.4	
18 AUGUST	WATER WHITE	7.0	0.060	11.0	



COLOR: TAN
pH = 2.3
DISSOLVED SOLIDS = 0.3%
CHLOROFORM-EXTRACTABLE MATTER = 57.6 PPM
8 JUNE 1970

COLOR: CLEAR
pH = 6.5
DISSOLVED SOLIDS = 0.20%
CHLOROFORM-EXTRACTABLE MATTER = 266.5 PPM
22 JUNE 1970

COLOR: RED
pH = 11.4
DISSOLVED SOLIDS = 2.00%
CARBON-TETRACHLORIDE-EXTRACTABLE MATTER = 78.9 PPM
23 JULY 1970

COLOR: GREEN FLUORESCENT
pH = 8.3
DISSOLVED SOLIDS = 0.07%
CARBON-TETRACHLORIDE-EXTRACTABLE MATTER = 39.9 PPM
13 JULY 1970

EACH SPECTRUM IS ANNOTATED WITH (1) OUTFALL COLOR, (2) OUTFALL pH, (3) % DISSOLVED SOLIDS, (4) QUANTITY OF "OILS" EXTRACTABLE WITH CHLORINATED SOLVENTS, AND (5) SAMPLING DATE.

NO TWO SPECTRA IN THIS FIGURE ARE THE SAME, THEREBY ILLUSTRATING THE VAST VARIABILITY IN POLLUTANTS PRESENT IN THE DISCHARGES OF THIS INDUSTRY (NATIONAL ANILINE DIVISION).

Figure 71 INFRARED SPECTRA CHARACTERIZING THE SOLVENT-EXTRACTABLE OILY POLLUTANTS IN SAMPLES OF HIGHLY VARIABLE OUTFALLS FROM A MAJOR CHEMICAL PLANT OVER A 2-MONTH PERIOD (JUNE AND JULY 1970) (SHEET 1 OF 2)

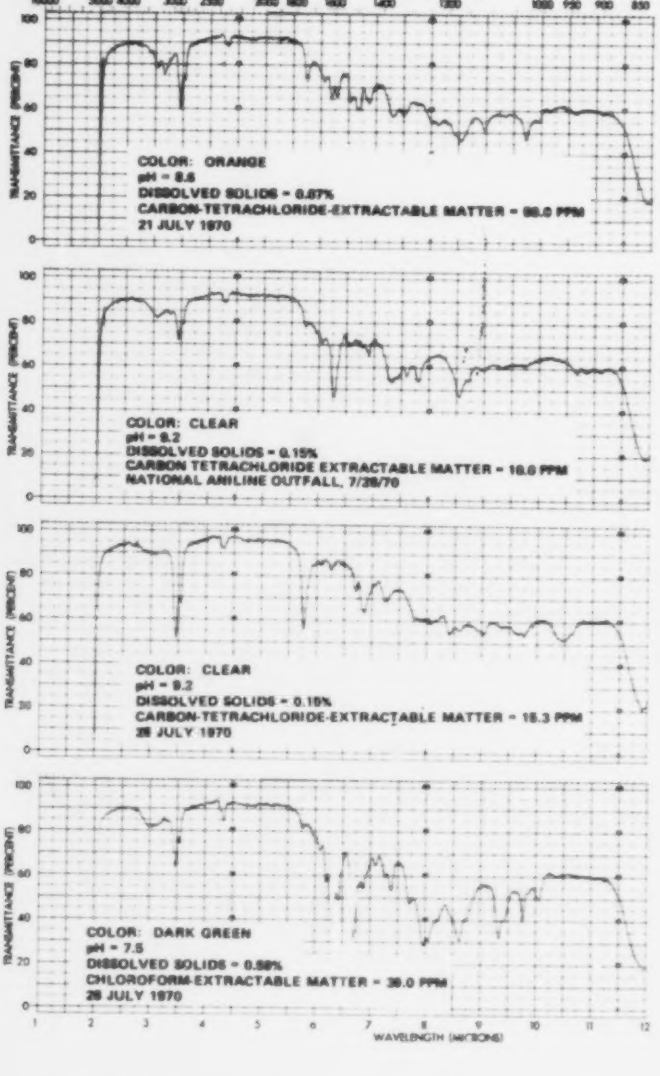


Figure 71 INFRARED SPECTRA CHARACTERIZING THE SOLVENT-EXTRACTABLE OILY POLLUTANTS IN SAMPLES OF HIGHLY VARIABLE OUTFALLS FROM A MAJOR CHEMICAL PLANT OVER A 2-MONTH PERIOD (JUNE AND JULY 1970) (SHEET 2 OF 2)

innocuous outfall and one not worthy of further investigation. However, the chloroform-extractable matter in this apparently clean industrial outfall was 246.5 ppm, an extreme deviation from any acceptable norm.

Table 17 lists analytical information on industrial outfalls of much more constant quality as collected over the 1970 sampling season. These typify the industrial effluents from a steel plant, an oil refinery, a granary, a major air fractionating plant, and a heavy equipment manufacturing plant.

Figure 72 presents infrared spectra which characterize the solvent-extractable oily pollutants typically found in the outfalls from the steel plant, the oil refinery, and the heavy equipment manufacturer during 1970. One will note from inspection of these spectra that they are all qualitatively similar, indicating the presence of oxidized hydrocarbons suspended or emulsified in the bulk water phase.

Table 18 represents an attempt to correlate the quality of the outfalls with the simplest visual parameter, namely color. Inspection of the table indicates the failure of this approach. Any particular color may be due to a mixture of many wastes from many different manufacturing processes or precursors. The outfalls tabulated in Table 18 do represent a significant input to the River in the industrial section and have a very wide range of pH values. It is interesting to note, as we have earlier in this report, that the Buffalo River bulk water samples have a much narrower pH range (approximately 6.5 through 7.5). This observation indicates the buffering capacity of this watercourse in that it contains sufficient organic materials to appropriately complex or otherwise interact with the pH-varying discharges of the industries to negate their effect on the pH of the River as a whole.

Figure 73 plots the pH level observed in any given industrial effluent against the percent dissolved solids observed simultaneously and demonstrates that as the fluctuations in water pH grow very extreme so do the fluctuations in dissolved solids. Thus, lack of control of the water quality in terms of one parameter generally indicates similar lack of control for all parameters.

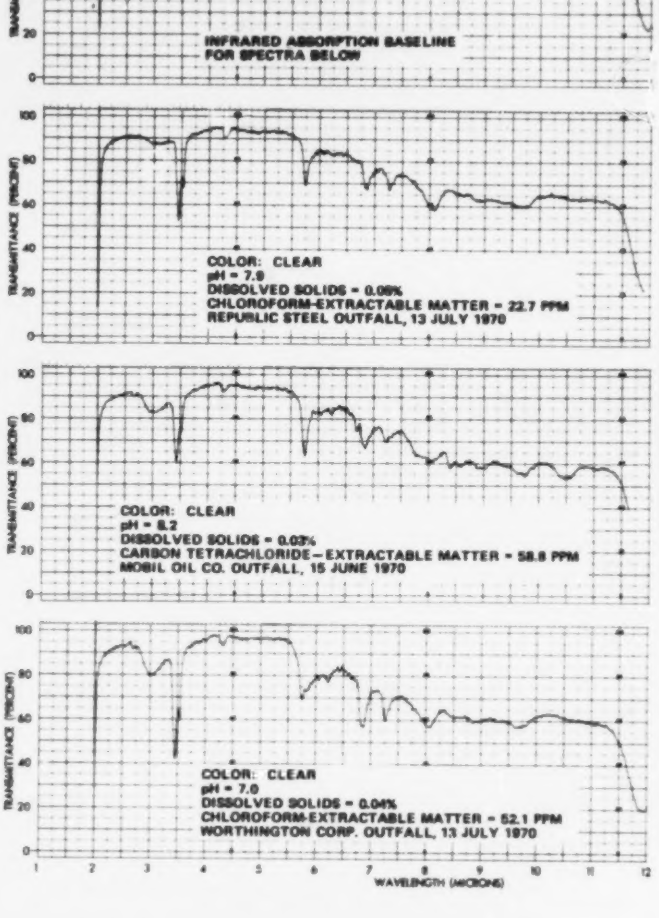
CORRELATION OF OUTFALLS BY THEIR ULTRAVIOLET SPECTRA

A study of the ultraviolet spectra of the various industrial outfalls revealed certain details. Spectra of at least 16 outfall samples were amenable to fitting to only four basic ultraviolet spectra (spectra recorded over the 200 - 350 nanometer range). These typical spectral shapes and the characteristics of the outfalls they correlate with appear on Figure 74 through Figure 77. Of the eight outfalls typified by spectral type number I, all but one were found to have pH levels in excess of 10.0. Indeed six of the eight had pH levels in excess of 11. The same six had chloroform extractable material present in at least 30 ppm concentrations, while their dissolved solids in each case exceeded 1/4%. The second set of outfalls including only two

Table 17

CHARACTERIZATION OF INDUSTRIAL OUTFALLS OF REASONABLY CONSTANT QUALITY OVER 1970 SAMPLING SEASON

DATE (1970)	COLOR	pH	% DISSOLVED SOLIDS	EXTRACTABLES (PPM)	
				CHLORO-FORM	CARBON TETRA-CHLORIDE
STEEL COMPANY OUTFALLS					
11 MAY	WATER WHITE	6.7	0.028	36	
25 MAY	WATER WHITE	7.1	0.032	64.8	
1 JUNE	WATER WHITE	6.8	0.032	67.4	
15 JUNE	WATER WHITE	8.0	0.048		17.0
13 JULY	WATER WHITE	7.9	0.046	22.7	
11 AUGUST	WATER WHITE	6.8	0.086	18.1	
11 AUGUST	WATER WHITE	6.6	0.050	21.5	
OIL COMPANY OUTFALLS					
15 JUNE	WATER WHITE	8.2	0.034		58.6
11 AUGUST	WATER WHITE	7.3	0.125	15.5	
25 AUGUST	WATER WHITE	7.0	0.048	29.2	
GRANARY OUTFALL					
15 JUNE	WATER WHITE	8.2	0.050		21.7
AIR FRACTIONATING PLANT OUTFALL					
13 JULY	WATER WHITE	7.9	0.072	24.7	
HEAVY MANUFACTURER'S OUTFALL					
13 JULY	WATER WHITE	7.0	0.036	52.1	



NOTE: ALL SPECTRA RECORDED ARE QUALITATIVELY SIMILAR, INDICATING THE PRESENCE OF OXIDIZED HYDROCARBONS SUSPENDED OR EMULSIFIED IN THE BULK WATER PHASE

Figure 72 INFRARED SPECTRA CHARACTERIZING THE SOLVENT-EXTRACTABLE OILY POLLUTANTS TYPICALLY FOUND IN OUTFALLS FROM A STEEL PLANT, AN OIL REFINERY, AND A HEAVY EQUIPMENT MANUFACTURER DURING THE 1970 SAMPLING PROGRAM ON THE BUFFALO RIVER

Table 18

CHEMICAL PLANT OUTFALLS TABULATED BY COLOR

DATE (1970)	pH	% DISSOLVED SOLIDS	EXTRACTABLES (PPM)	
			CHLORO-FORM	CARBON TETRA-CHLORIDE
YELLOW SPECIMENS				
20 APRIL	8.4	22.2		39.5
18 MAY	11.8	0.382		65.4
25 MAY	11.2	0.254		71.2
8 JUNE	11.4	0.216		19.2
15 JUNE	3.5	0.112	25.6	
RED SPECIMENS				
20 APRIL	3.9		5.0	
8 JUNE	2.9	0.168	32.9	
22 JUNE	3.9	0.175	35.0	
13 JULY	11.4	2.002		78.9
TAN SPECIMENS				
18 MAY	5.3	0.056	73.3	
8 JUNE	2.3	0.304	57.6	
6 JULY	11.9	0.276		47.6
21 JULY (#2)	8.7	0.128		28.5
GREEN SPECIMENS				
20 APRIL	9.1			3.0
15 JUNE	8.7	0.006		22.3
22 JUNE	2.0	0.177	25.3	
13 JULY*	8.3	0.065		39.9
28 JULY	7.5	0.590	39.0	

*FLUORESCENT

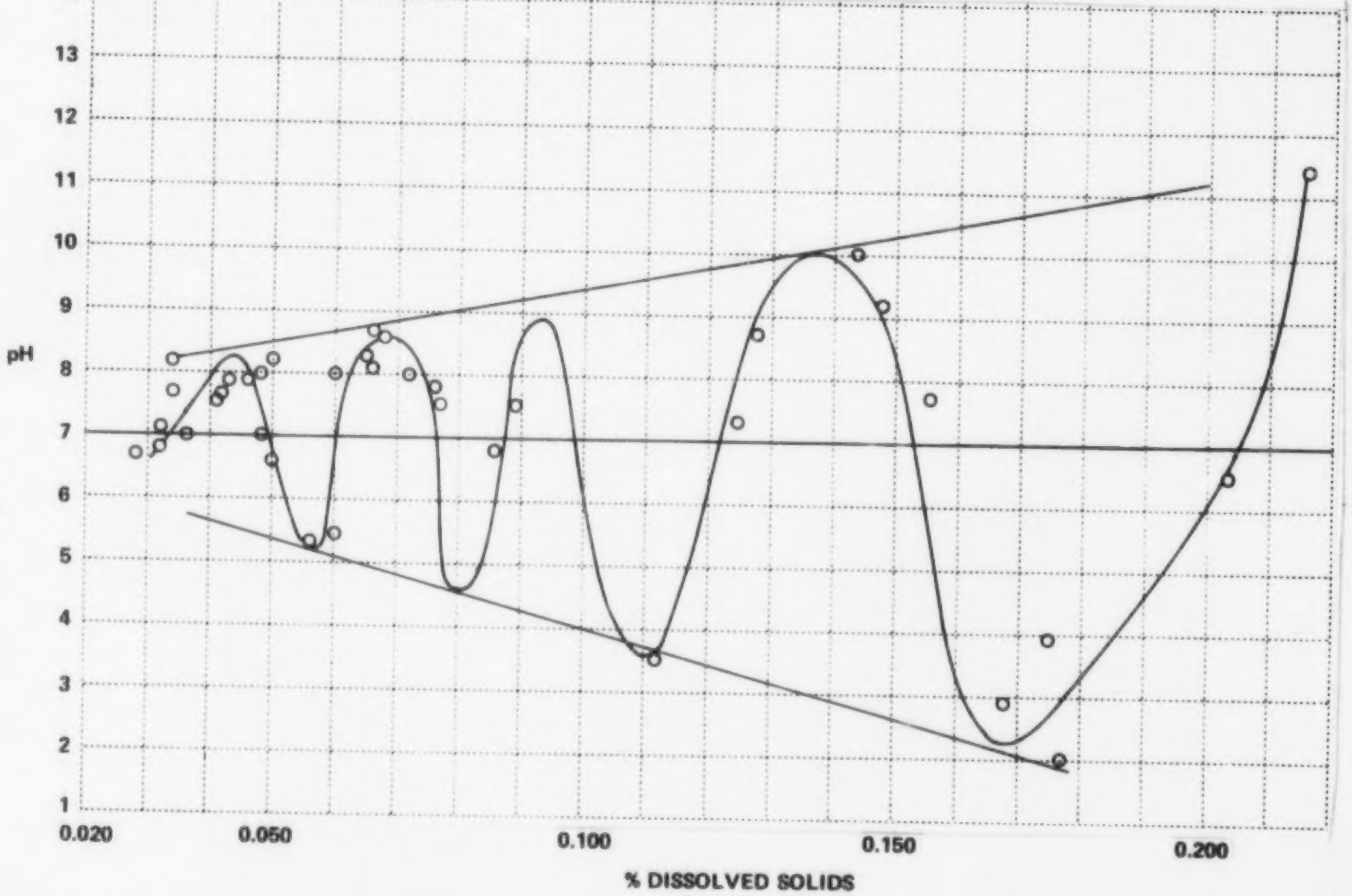
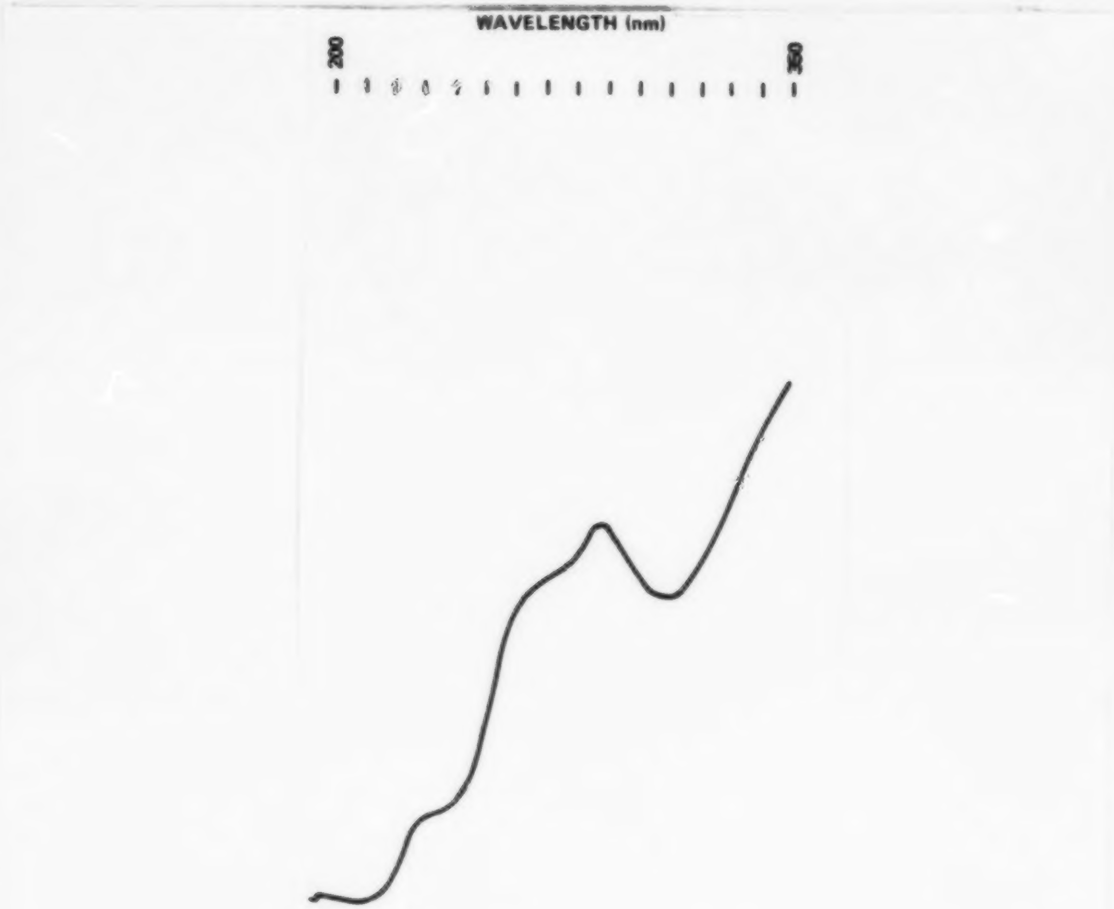


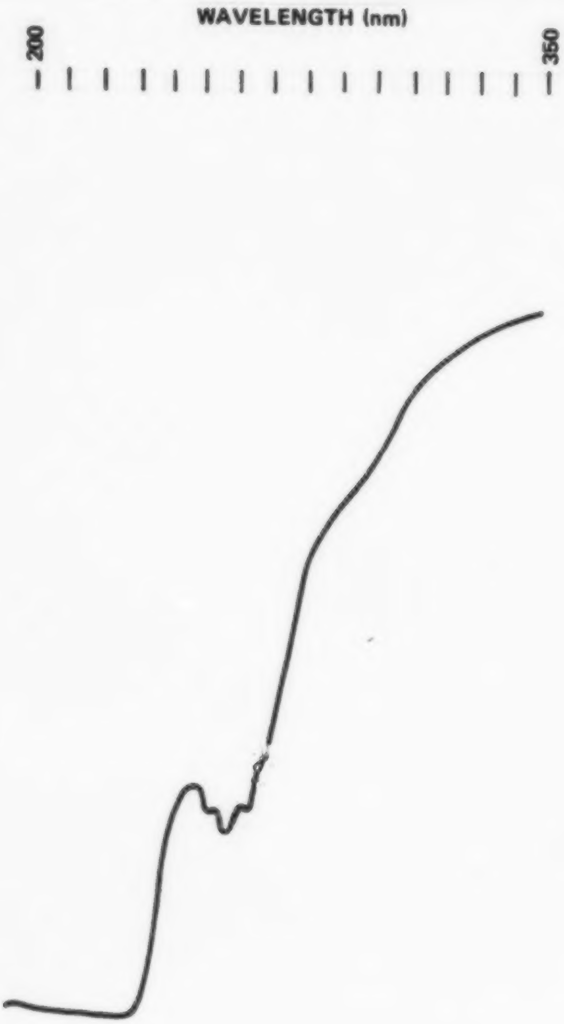
Figure 73 PLOT OF OUTFALL DISSOLVED SOLIDS VS. pH



SOURCE	DATE (1970)	COLOR	pH	SOLIDS (%)	EXTRACTABLES (PPM)	
					CHLOROFORM	CARBON TETRACHLORIDE
CHEMICAL PLANT	18 MAY	YELLOW	4.8	0.382	65.4	
CHEMICAL PLANT	15 JUNE	YELLOW	12.1	0.487		50.6
CHEMICAL PLANT	13 JULY	RED	11.4	2.002		78.9
CHEMICAL PLANT	13 JULY	W/W*	7.5	0.077	25.3	
CHEMICAL PLANT	13 JULY	W/W*	10.0	0.144		15.3
CHEMICAL PLANT	22 JUNE	YELLOW	12.0	0.492		38.2
CHEMICAL PLANT	6 JULY	LT TAN	11.9	0.276		47.6
CHEMICAL PLANT	6 JULY	PINK	12.1	0.278		31.6

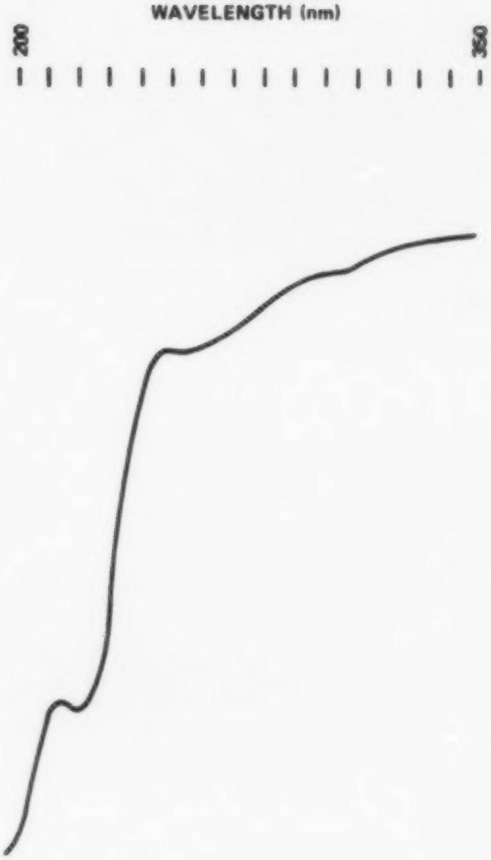
*WATER-WHITE

Figure 74 ULTRAVIOLET SPECTRUM TYPE I AND LISTING OF OUTFALLS TYPIFIED BY THIS SPECTRAL SHAPE



SOURCE	DATE (1970)	COLOR	pH	SOLIDS (%)	CHLOROFORM EXTRACTABLES (PPM)
CHEMICAL PLANT	22 JUNE	GREEN	2.0	0.177	25.3
CHEMICAL PLANT	22 JUNE	WATER WHITE	6.5	0.204	246.5

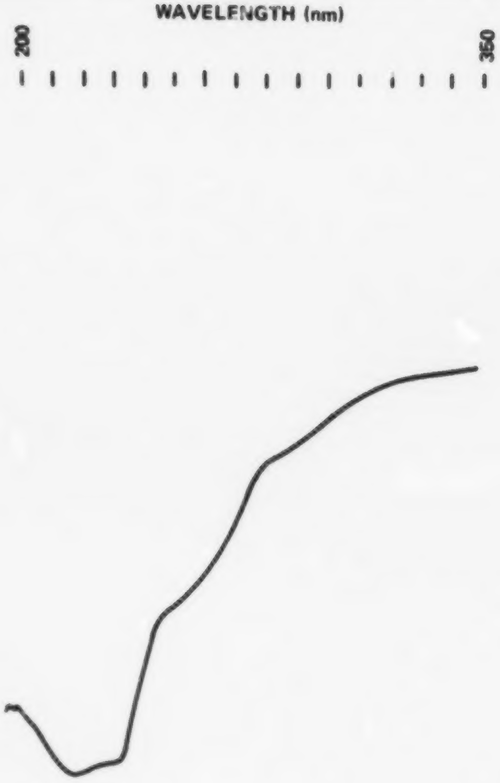
Figure 75 ULTRAVIOLET SPECTRUM TYPE II AND LISTING OF OUTFALLS TYPIFIED BY THIS SPECTRAL SHAPE



SOURCE	DATE (1970)	COLOR	pH	SOLIDS (%)	CHLOROFORM EXTRACTABLES (PPM)
CHEMICAL PLANT	18 AUGUST	W/W*	7.0	0.060	11.0
SURFACE FOAM	18 AUGUST	W/W*	7.1	0.076	14.3

*WATER-WHITE

Figure 76 ULTRAVIOLET SPECTRUM TYPE III AND LISTING OF OUTFALLS TYPIFIED BY THIS SPECTRAL SHAPE



SOURCE	DATE (1970)	COLOR	pH	SOLIDS (%)	EXTRACTABLES (PPM) CHLOROFORM	EXTRACTABLES (PPM) CARBON TETRACHLORIDE
CHEMICAL PLANT	8 JUNE	TAN	2.3	0.304	57.6	
CHEMICAL PLANT	8 JUNE	RED	2.9	0.168	32.9	
CHEMICAL PLANT	15 JUNE	YELLOW	3.5	0.112	25.6	
CHEMICAL PLANT	21 JULY	ORANGE	8.6	0.068		50.0

Figure 77 ULTRAVIOLET SPECTRUM TYPE IV AND LISTING OF OUTFALLS TYPIFIED BY THIS SPECTRAL SHAPE

illustrations yielded less correlation. Note, however, that the second water-white sample had a chloroform extractable concentration an order of magnitude greater than the colored sample, illustrating that effluent color does not always correlate with its degree of oily pollution.

Spectral shape III also characterizes only two samples, both from the chemical plant. One sample represents a clear water outfall and the other sample an abundant amount of white surface foam formed on the Buffalo River surface adjacent to this outfall.

Spectral shape IV, representing four separate outfalls, again shows a lack of correlation of outfall quality with actual color of the outfall. One point of obvious difference among these samples is that three of the four samples have a pH of less than 4.0, very much on the acid side, whereas the fourth sample has a basic pH greater than 8.0. Also, one will note the decrease of dissolved solids and chloroform extractable material as the pH approaches neutrality in the first three samples listed on Figure 77.

ADDITIONAL OBSERVATIONS

Other observations were also made during the course of chemical analysis of outfall samples, some after adventitious combinations of materials. For example, the mixing of two outfalls of widely differing pH often caused the evolution of a gas that had a very strong hydrogen sulfide odor. Other observations of the ready spreadability of the extracted oils from certain of the industrial effluents attested to their very high "surface pressure" and might eventually be found to correlate with the presence of deliberate emulsifiers or surfactants added to keep these materials suspended in the water phase. It was not considered within the scope of the present study to perform the detailed chemical analyses of the various effluents which would be required to extend and confirm these occasional observations.

SAMPLING AND IDENTIFICATION IN SUPPORT OF THE AIR BARRIER EVALUATION

During the 1969 sampling season on the Buffalo River, surface film samples directly over the air barrier and in the film stagnation regions about 20 meters upstream and downstream from the barrier were retrieved by use of the prism-dip technique and the surface active hoop technique described earlier in this report. The air barrier was not operated continuously so samples were obtained only for limited times of operation of the air curtain. The infrared spectra shown in Figure 78 are typical of samples both within the bubble zone where the current was driving the oily pollutants laterally away from the curtain center and in the stagnation zone itself where the surface film was noted to collect.

The infrared spectra of these samples are strikingly different from other spectra characterizing the surface films over the rest of the Buffalo River. As indicated in the figure, a large proportion of the normal aliphatic oil content observed over the entire length of the Buffalo River was apparently efficiently oxidized in the region of the air barrier to compounds containing hydroxyls, esters, carbon-carbon double bonds, and alcohols. The vigorous bubbling action was apparently responsible for the oxidation. In addition to introducing such double bond, alcoholic and aldehydic groups into the hydrocarbon pollutants themselves, the air barrier was also very likely breaking up an emulsion of similarly oxidized pollutant substances normally suspended as stable micelles in the bulk water. Two prominent features are apparent in Figure 78. Within the air barrier bubble zone no surface film collects to any great degree. Only small residual peaks are noted in what are commonly considered the amide I and amide II regions near 1650 cm^{-1} and 1550 cm^{-1} in the top trace in this figure. In the lower trace, typifying the stagnation point film, there are very large and prominent amide bands at these positions, indicating that the initial operation of the air barrier contributed very rapidly to the accumulation and concentration of proteinaceous materials which were originally suspended in the bulk water.

During the 1970 sampling season, as already noted in earlier sections of this report, surface oil samples and surface water samples were collected along the entire length of the Buffalo River. To aid specifically in the evaluation of the performance of the pneumatic barrier, surface samples were collected every few meters on each side of the air barrier with emphasis on detecting the oil accumulation in and about the stagnation zones formed by the barrier's pneumatic action. Unfortunately, the barrier was originally installed in one of the least surface-polluted areas of the river. Yet, preliminary data by surface screen sampling showed that even after only three hours of barrier operation the content of chloroform-extractable matter in the surface screen samples increased markedly. Thus, numerous surface film samples

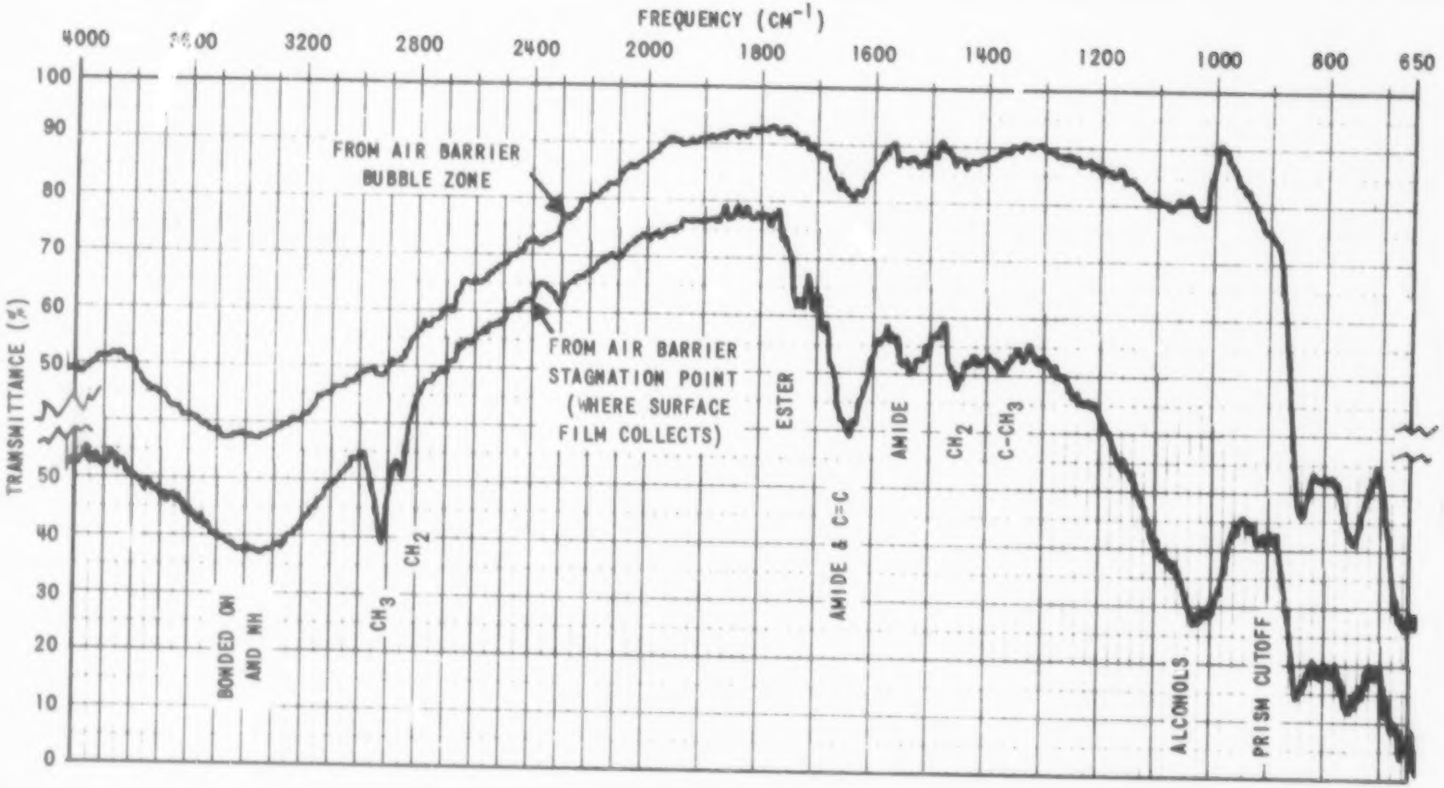


Figure 78 INFRARED EVIDENCE FOR EXTENSIVE OXIDATION OF HYDROCARBONS AND FOR BRINGING UP OF DISSOLVED PROTEINS AND EMULSIFIED COMPONENTS (OXIDIZED HYDROCARBONS) IN BULK WATER DUE TO BUBBLING ACTION OF PNEUMATIC BARRIER

were obtained and also samples of the immediate subjacent surface water (using the surface screen technique), the analyses of which are the major subject of this section.

Dissolved oxygen content and water temperature were also measured as indicators of the air barrier influence on the water quality in the adjacent sections of the stream from a few meters to many hundreds of meters upstream and also as compared with locations a half mile to a full mile up- and downstream of the air barrier. The dissolved oxygen content measured just below the water surface and at a depth of two feet, and the water temperatures about a half foot below the surface, showed striking changes in the character of the river water as far as 100 meters both upstream and downstream of the air barrier. A lengthy sequence of measurements was performed during the period of 18 May through 27 May 1970 while the air barrier was kept in continuous operation for ten full days. During the temperature study, a notation of substantial cooling of the surface waters was no doubt partially due to the upwelling of cooler subsurface water by the air column from the barrier, as well as to higher evaporation due to the bubble breaking at the air barrier centerline.

In preparation for the ten-day period of extensive sampling at the air barrier, equilibrium conditions were established by allowing the air barrier to operate continuously for half a day on 11 May before collecting surface, subsurface, and bulk water samples. Eight surface screen samples, averaging a minimum of ten dips each in the water surface, were collected on that day as well as a number of bulk water samples at the three-meter depth. Further, surface-active hoop samples were collected from five to one hundred meters up- and downstream of the operating air barrier. Eight samples of this type were collected and analyzed. On May 18 the ten-day long period of continuous operation and evaluation of the air barrier commenced in anticipation of assessing the performance of the barrier during the highest flow likely to be encountered in the Buffalo River during that particular spring season. Twenty separate surface screen samples were taken at various distances up- and downstream from the operating air barrier on 18 May 1970. For comparison, surface-active hoop samples were also taken up- and downstream to the 150 meter mark in both directions from the air barrier and at a number of sampling sites up and down river during that sampling day. Twelve samples of bulk water were collected and analyzed at these various distances ranging in depth from one meter to three meters. Finally, four separate samples of bottom water were taken and their chloroform-extractable organic pollutants estimated. Two days later on 20 May, twelve additional surface screen average samples were collected up- and downstream of the barrier and eight additional up- and downstream surface-active hoop samples were collected and analyzed. On 25 May twelve surface screen average samples were collected along with eight surface-active hoop samples of the floating oil pollutant films themselves. The final sampling date (27 May 1970 - the tenth complete day of continuous operation) saw twelve surface screen samples taken at distances between 5 and 150 meters up- and downstream of the barrier, and six surface-active hoop samples were taken at the same time. On the sampling days, the pH excursions were never large and always centered on neutrality. On 11 May, the minimum pH noted was 6.8; the maximum was 7.2. The same range was noted on 18 May, with the exception of three samples on the lower pH side, 6.8, and one at 6.6. On 20 May, the pH of all the water samples ranged from a low of 5.2, which was an exceptionally low value found 20 meters downstream of the barrier, to a high of 7.1. On 25 May, the pH range was 6.8 to 7.2, and on the final sampling day, 27 May, the pH range was 6.6 to 7.0.

Over the course of the extensive ten-day sampling program, the weather and winds varied markedly. On the preliminary experiment of 11 May, the wind was from the WSW at about 13 mph, the day was sunny, and the mean river flow through the Michigan bridge site (air barrier site) was estimated to be 490 ft^3/sec from figures provided to us by the U.S. Geological Survey Office. On 18 May, the wind was out of the WSW at 9 mph and clear skies prevailed throughout sampling. However, it had rained on the previous day and the mean river flow was estimated to be 867 ft^3/sec. Two days later, the wind was from the NNE at 7 mph and the day was sunny. No rain had fallen since the previous sampling day and the mean river flow had accordingly dropped to 457 ft^3/sec. Five days later, on 25 May, the wind was out of the SW at 10 mph and the day was partly cloudy with occasional showers throughout the sampling period. A steady rain the day before, on 24 May, had augmented the runoff into the River such that its mean flow was estimated to be 707 ft^3/sec. On the final sampling day, 27 May, the winds were NW and gusting. The water surface was very rough and readily mixed by the gusting winds. Very heavy rains on the previous day, 26 May, had augmented the mean river flow to an estimated 800 ft^3/sec.

When comparisons were made among the amounts of chloroform-extractable matter in the water samples up and downstream of the operating air barrier (from the bottom to the surface waters), it immediately became clear that the surface samples (taken by the surface screen in the immediate vicinity of the air barrier and by the surface-active hoop [collecting the obvious pollutant films floating above the water surface]) were the most graphical indicators of any effect of the pneumatic barrier operation. These samples showed a rather high concentration of surface burden at the points where the barrier-induced counter current was exactly cancelled by the combination of the stream's natural current and the prevailing winds on any given day. The pollutant burden, emulsified or suspended in the bulk waters at any distance from slightly below the surface all the way down to the bottom waters, apparently passed through the bubble curtain unmodified. Although there was a dramatic increase of dissolved oxygen in those same water layers, no long-term reduction of the chemical oxygen demand of the bulk water was found.

Table 19 is a compilation of the air barrier sampling data on the surface "film oils," the surface water "emulsified oils," and the dissolved oxygen at the River surface and at the two-foot depth in the River in the vicinity upstream and downstream of the operating air barrier on the five major sampling dates already listed.

Figure 79 gives a sequence of infrared spectra characterizing (a) the chloroform-extractable matter in the surface films which were prevented from passing the counter current of the air barrier, and (b) the surface water adjacent to the air barrier during the 10 days of continuous pneumatic operation. Inspection of these spectra will show that the surface film components underwent an apparent progressive increase in their state of oxidation with increasing time of operation of the air current. Evidence for the increasing state of oxidation for these hydrocarbon materials may be found in the ester bands at approximately 1750 cm^{-1} and with the carboxylated hydrocarbons having peaks around 1300, 1200, and 1100 cm^{-1}. It will also be noted, from inspection of the bottom trace in Figure 79, that the surface water samples, of which this is a typical example, all showed a very high proportion of oxidized hydrocarbons. Further, it was noted in the laboratory that upon standing for even a few hours all such samples became rancid by rapid action of the bacteria in this nutritious, highly oxygenated broth. Contrasting this spectrum, and indeed all other spectra in Figure 79, with the spectra in Figure 78, it can be seen that the continuous operation of the air barrier over a few days time apparently stripped all of the available proteinaceous material from the adjacent waters. Thus, concentration of proteinaceous materials in the surface films was not apparent during this 1970 sampling program.

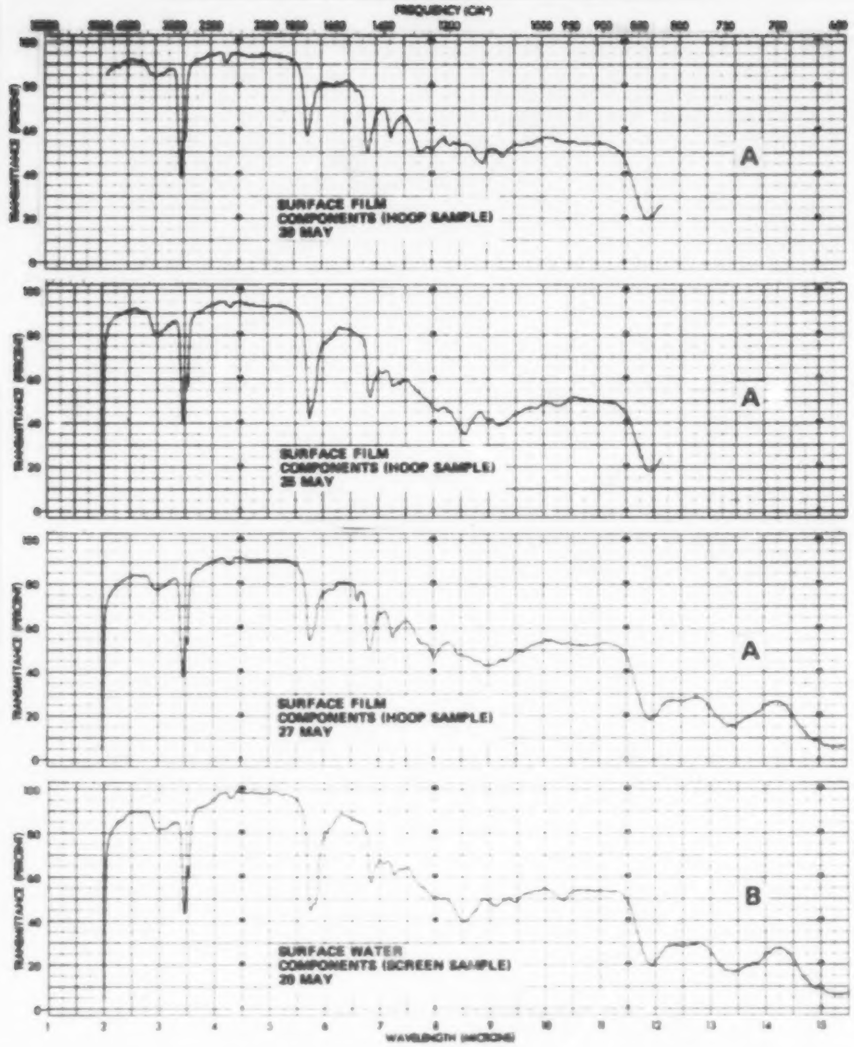
Figures 80 and 81 present distance vs. concentration profiles for the surface screen samples and surface-active hoop samples, respectively, taken during operation of the air barrier over the ten-day period.

The constant infusion of air in the air barrier zone (in and adjacent to the rising air curtain) was expected to, and the following figures demonstrate that it did, have a large effect on both the surface temperature and the dissolved oxygen content in the area of the air barrier. Figure 82 contains plots of the water temperature and the dissolved oxygen content at the surface and at two-foot depths during continuous operation of the air barrier over the ten-day experimental period. Note in these plots that even 150 meters upstream from the air curtain itself the surface water was still reasonably well-oxygenated. As earlier sections of this report have shown, the bulk river water entering this particular region of the River was always seriously depleted of oxygen. On the other hand, at the 150 meter downstream mark, the two-foot depth samples for dissolved oxygen usually showed an amplified increase in oxygen influenced by occasional mixing with the better oxygenated lake water which occasionally reached this far upriver. In none of the data sets did the upstream dissolved oxygen ever exceed the dissolved oxygen spike noted immediately above

Table 19

COMPILATION OF AIR BARRIER SAMPLING DATA ON SURFACE FILM "OILS," SURFACE WATER "EMULSIFIED OILS," AND DISSOLVED OXYGEN AT SURFACE AND AT 2-FOOT DEPTH

DATE (1970)	DISTANCE UPSTREAM (m)						AT PNEUMATIC BARRIER	DISTANCE DOWNSTREAM (m)						DATA REPRESENT
	150	100	50	20	10	5		5	10	20	50	100	150	
11 MAY			2.1	29.5	45.5	24.5		13.0			29.5	25.0		CHLOROFORM-EXTRACTABLE MATTER IN SURFACE SCREEN SAMPLES (ppm)
18 MAY	2.0	1.3	1.8	2.1	1.4	>1.0			2.3	2.0	2.2	2.5		
20 MAY	3.7	2.4	3.9	2.1	2.4	2.6		2.4	2.6	37.9	2.6	1.0		
25 MAY		4.2	1.9	3.7	2.0	6.1		3.7	3.5	2.8	2.4	3.2	3.2	
27 MAY	9.7	6.9	8.9	7.2	16.8	7.3	4.7	1.9	3.1	3.8	3.7	4.1		
18 MAY	0.0274		0.0382	0.0355	0.0389					0.01985				CHLOROFORM-EXTRACTABLE MATTER IN SURFACE HOOP SAMPLES (g/m^2)
20 MAY		0.0194		0.0167	0.01485				0.0110	0.03175	0.01306	0.0157		
25 MAY			0.0442	0.01515	0.0524				0.0180	0.02205	0.0148	0.0185	0.0329	
27 MAY			0.0182	0.0202	0.0290				0.0155	0.0344				
20 MAY	4.4	4.5	4.7	5.2	5.7	5.8	5.5	6.5	5.7	5.7	5.7	5.8	5.4	DISSOLVED OXYGEN AT SURFACE (ppm)
25 MAY		0.7	0.4	0.6	0.5	2.5	4.0	3.2	2.0	1.9	1.4	3.0	1.6	
27 MAY	9.3	10.9	9.2	8.9	10.1	11.3	12.0	10.9	11.2	10.7	10.2	10.2	10.1	
20 MAY	3.3	4.5	4.8	4.8	5.3	5.2	5.1	6.8	5.3	5.5	5.5	5.2	5.0	DISSOLVED OXYGEN AT 2 FT DEPTH (ppm)
25 MAY		0.6	0.7	0.6	0.5	2.6	3.4	3.0	2.0	1.7	1.3	2.3	1.4	
27 MAY	9.2	10.3	9.0	10.0	10.0	11.6	12.8	11.1	11.3	10.9	10.2	10.3	9.7	



NOTE (1): SURFACE FILM COMPONENTS DEMONSTRATE AN APPARENT PROGRESSIVE INCREASE IN STATE OF OXIDATION WITH INCREASING TIME OF OPERATION OF AIR BARRIER.

NOTE (2): SURFACE WATER SAMPLES ALL SHOWED VERY HIGH PROPORTION OF OXIDIZED HYDROCARBONS, AND – UPON STANDING – ALL BECAME RANCID BY RAPID ACTION OF BACTERIA IN THIS NUTRITIOUS, HIGHLY OXYGENATED BROTH

Figure 79 INFRARED SPECTRA (A) CHARACTERIZING THE CHLOROFORM-EXTRACTABLE MATTER IN THE SURFACE FILMS PREVENTED FROM PASSING BY THE AIR BARRIER AND (B) TYPICAL OF THE SURFACE WATER ADJACENT TO THE AIR BARRIER DURING 10 DAYS OF CONTINUOUS OPERATION IN 1970

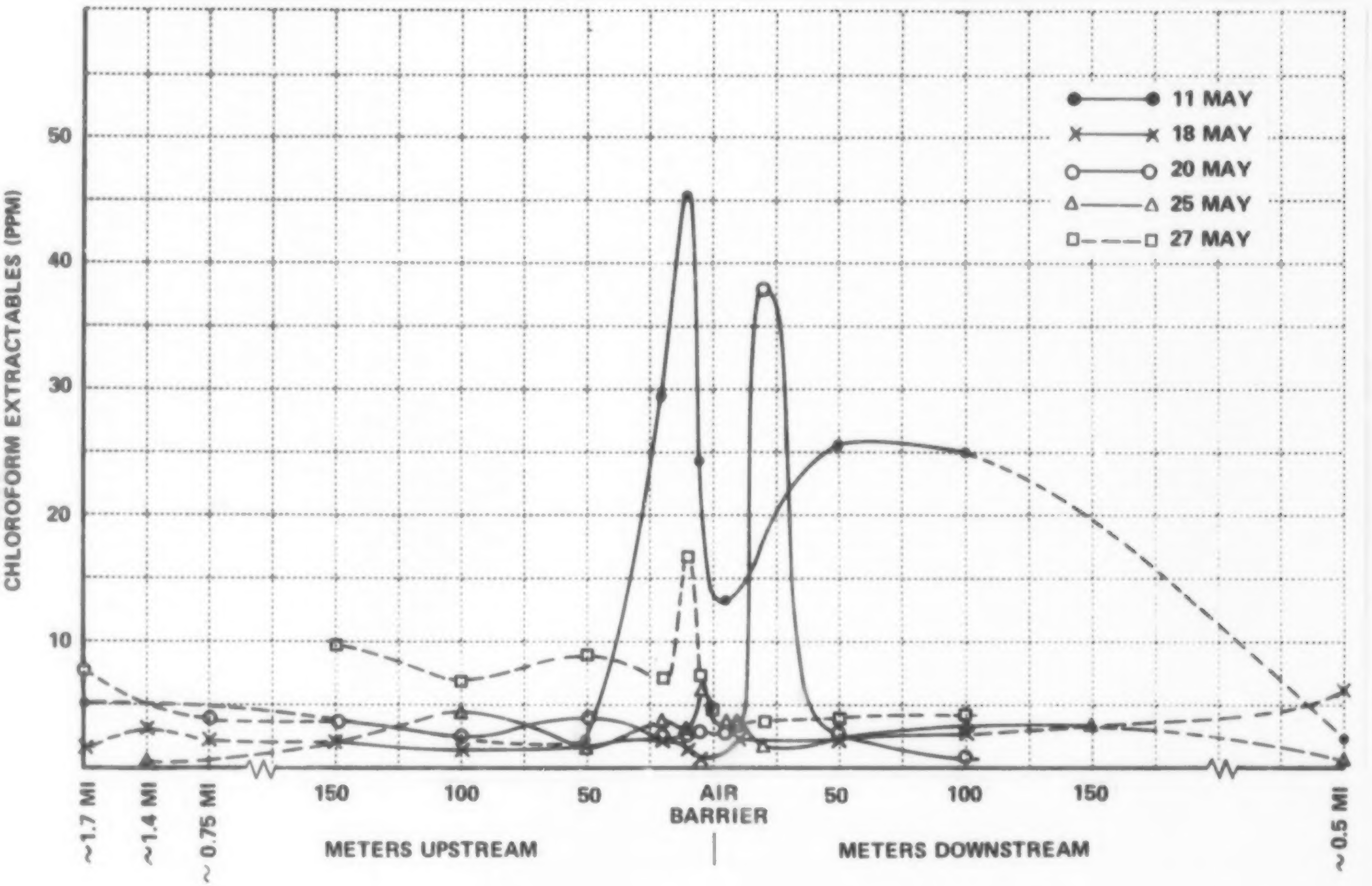


Figure 80 DISTANCE VERSUS CONCENTRATION PROFILES FOR SURFACE SCREEN SAMPLES COLLECTED DURING EVALUATION OF AIR BARRIER FOR 10 DAYS OF CONTINUOUS OPERATION IN 1970

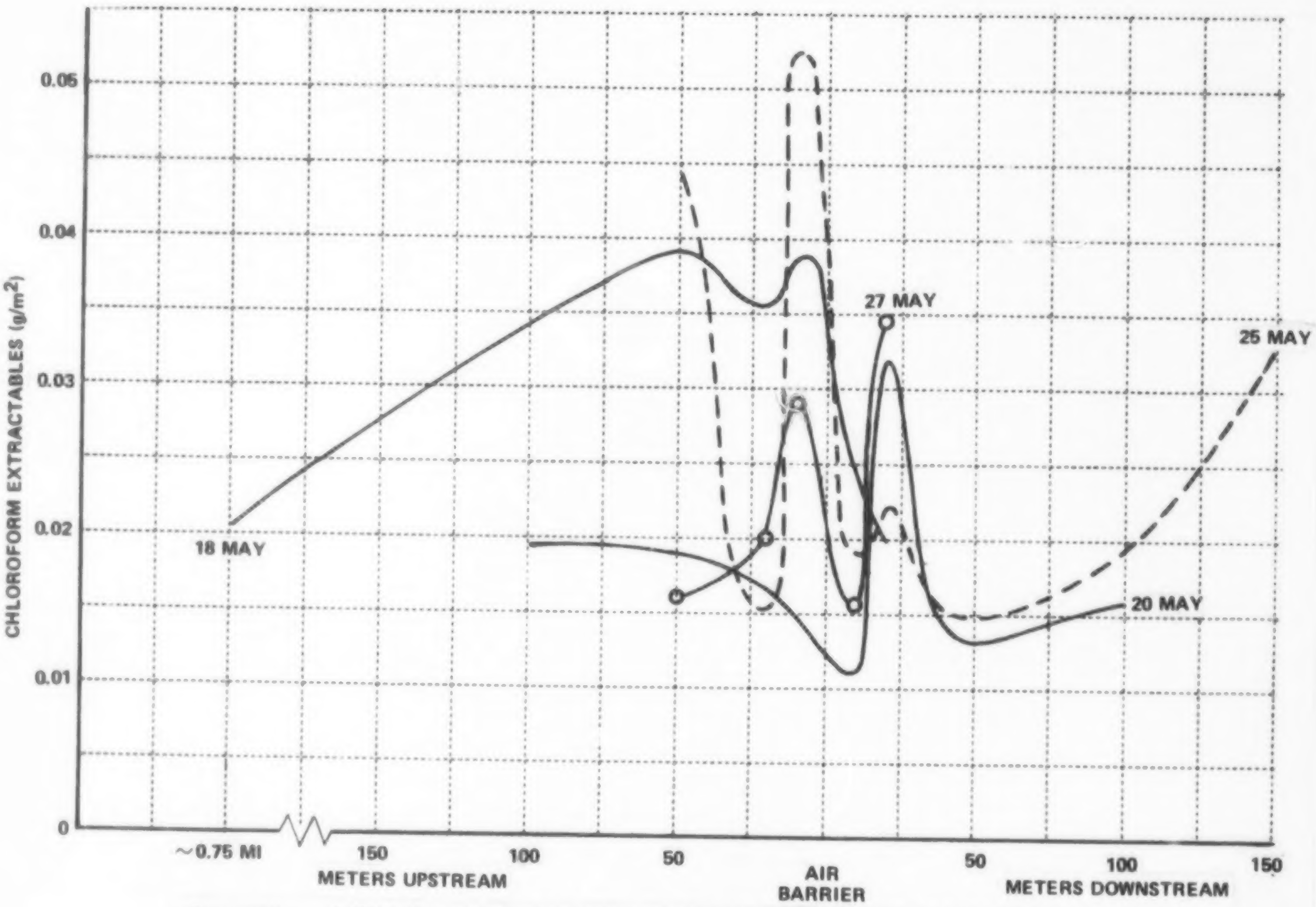


Figure 81 DISTANCE VERSUS CONCENTRATION PROFILES FOR SURFACE HOOP SAMPLES TAKEN DURING OPERATION OF AIR BARRIER OVER 10-DAY PERIOD IN 1970

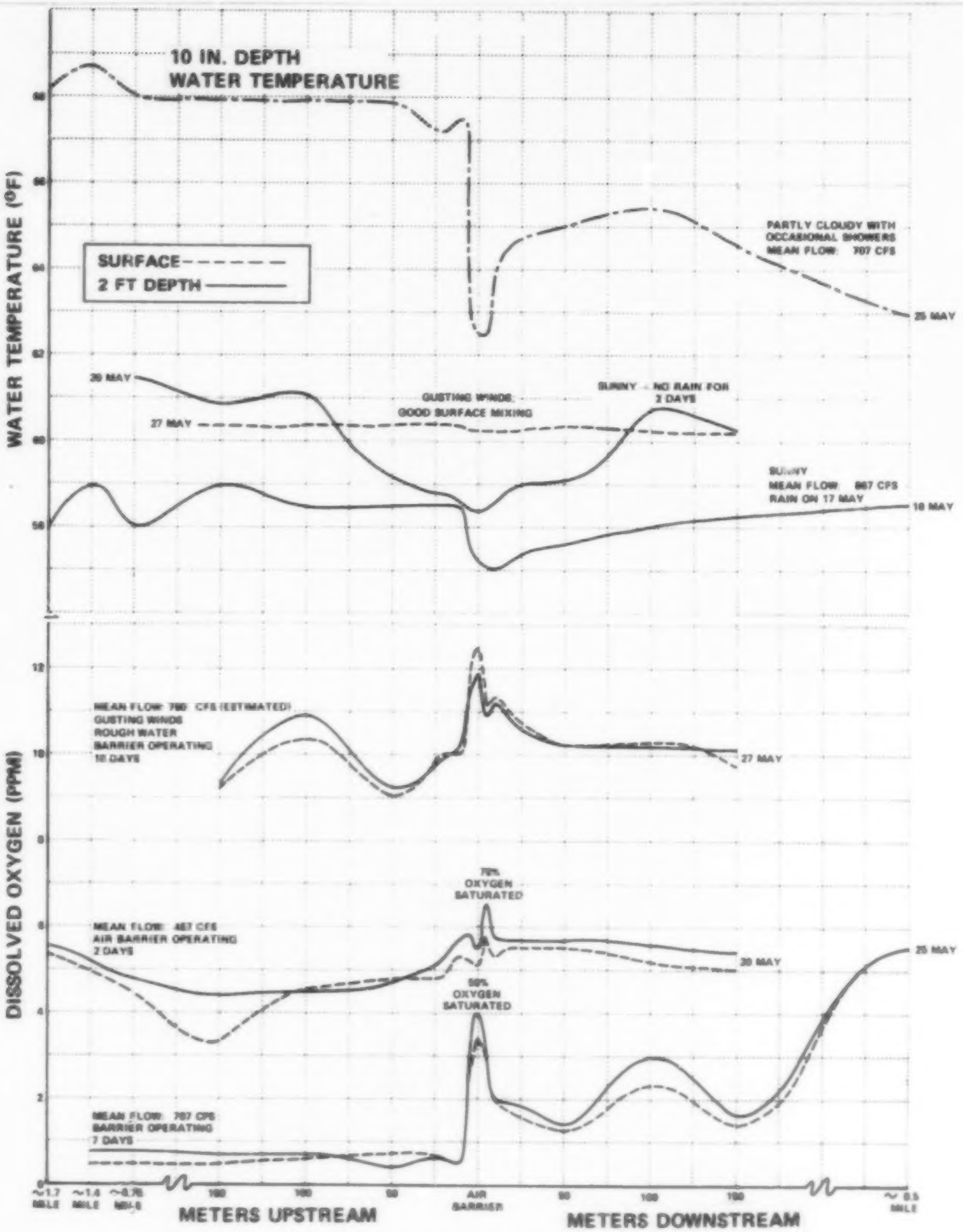


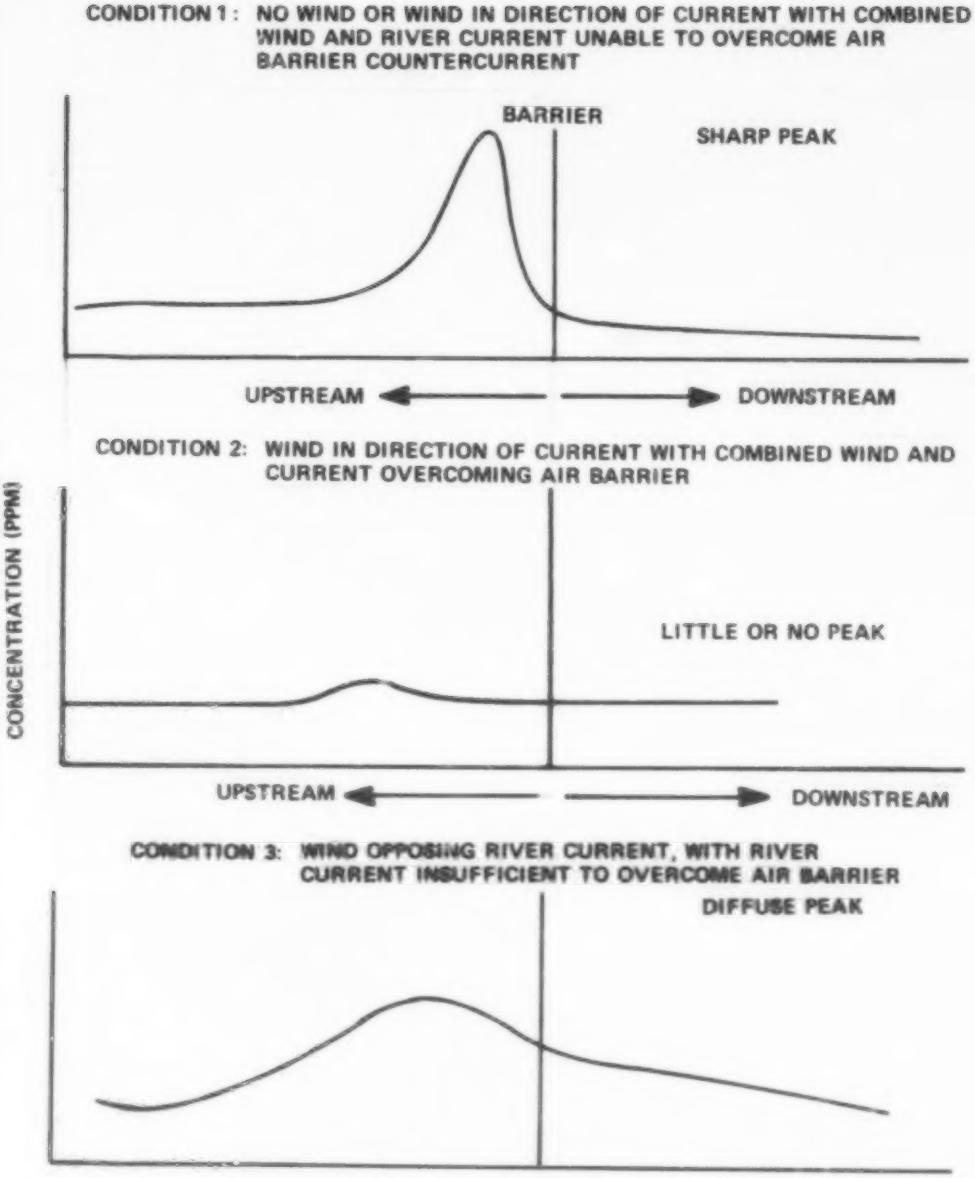
Figure 82 PLOTS OF WATER TEMPERATURE AND DISSOLVED OXYGEN CONTENT AT THE SURFACE AND AT 2 FT DEPTH DURING CONTINUOUS OPERATION OF AIR BARRIER OVER 10-DAY PERIOD IN 1970

the air barrier. On occasion this spike was exceeded in the half mile downstream samples, but as was already noted, the well stirred lake water is mixed with the River water at this point, thereby increasing the dissolved oxygen.

The information presented in Figure 82 strongly recommends additional programs of air barrier analysis -- programs, however, where a careful preselection has been made of the placement of the air barrier. In terms of the Buffalo River study completed over the past three years, the South Park Bridge site (Sample Site 5, shown in Figure 2) could be recommended as a superior site for an air barrier study. Since 1964, there has been a continuous body of data indicating that this site drops (in early summer) to 0% dissolved oxygen and has had a continuous history of very high chemical oxygen demand as well.

It was obvious to even casual observers that the pneumatic air barrier had the ability to entrap surface pollutants. Nowhere in the lower river segments did the surface concentration of pollutants (and the obvious slicks) reach the high magnitude of that in the immediate (plus or minus 20 meters) vicinity of the barrier under continuous operation. The presentation of these data in Figures 80 and 81, for the surface screen and surface-active hoop samples, respectively, might be taken on first glance to indicate a lack of correlation between the results determined by these two methods. However, the following paragraphs will demonstrate that these data were supplemental and convergent and did adequately describe the performance of the barrier over a variety of meteorological and flow conditions. A theoretical consideration of the pollutant profiles at and near the air barrier suggests that five conditions are possible: (1) no wind, or wind in direction of current with combined wind and river current unable to overcome air barrier countercurrent, (2) wind in direction of current with combined wind and river current overcoming air barrier, (3) a wind opposing the river current, but with the river current insufficient to overcome the counter current induced by the air barrier, (4) a wind opposing the river current, but with some oil passing through the air barrier zone due to sporadic failure of the air barrier counter current or strong wind gusts over the lake, (5) a wind opposing the river current, but with the river current overcoming the action of the air barrier and escaping downstream of it. When the stream current and the wind match one another, or mismatch one another in certain proportions, the pneumatic barrier can seem to become ineffective. Figure 83 shows schematic hypothetical pollutant profiles, theoretically expected during operation of an air barrier while variables in river currents and wind directions are being experienced.

Figures 84 and 85 plot the averages for the surface film concentrations and the surface water concentrations of oily pollutants, respectively, in the vicinity of the air barrier over ten days of its continuous operation. It will be noted that the plotted averages from both the hoop and the screen sampling tests have shapes approximating that



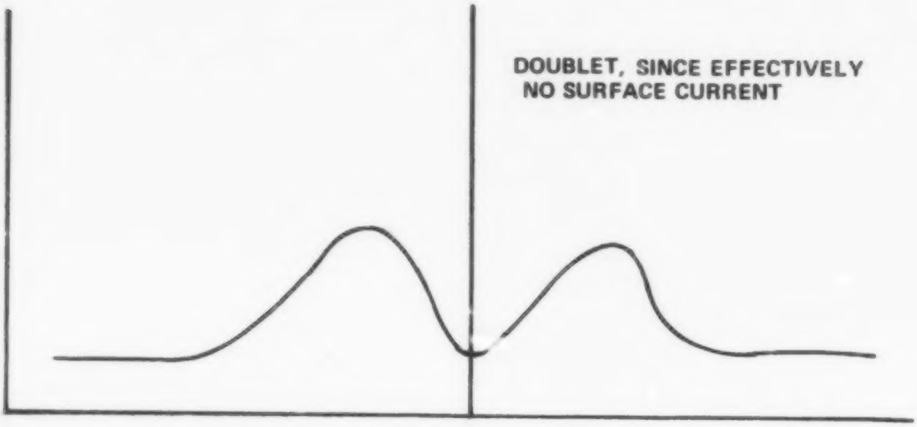
CONDITION 1: NO WIND OR WIND IN DIRECTION OF CURRENT WITH COMBINED WIND AND RIVER CURRENT UNABLE TO OVERCOME AIR BARRIER COUNTERCURRENT

CONDITION 2: WIND IN DIRECTION OF CURRENT WITH COMBINED WIND AND CURRENT OVERCOMING AIR BARRIER

CONDITION 3: WIND OPPOSING RIVER CURRENT, WITH RIVER CURRENT INSUFFICIENT TO OVERCOME AIR BARRIER

Figure 83 HYPOTHETICAL POLLUTANT PROFILES EXPECTED DURING OPERATION OF AIR BARRIER DURING PERIODS WITH VARIABLE RIVER CURRENTS AND WIND DIRECTIONS (SHEET 1 OF 2)

CONDITION 4: WIND OPPOSING RIVER CURRENT, WITH SOME OIL PASSING THROUGH AIR BARRIER ZONE



CONDITION 5: WIND OPPOSING RIVER CURRENT, WITH CURRENT OVERCOMING ACTION OF AIR BARRIER

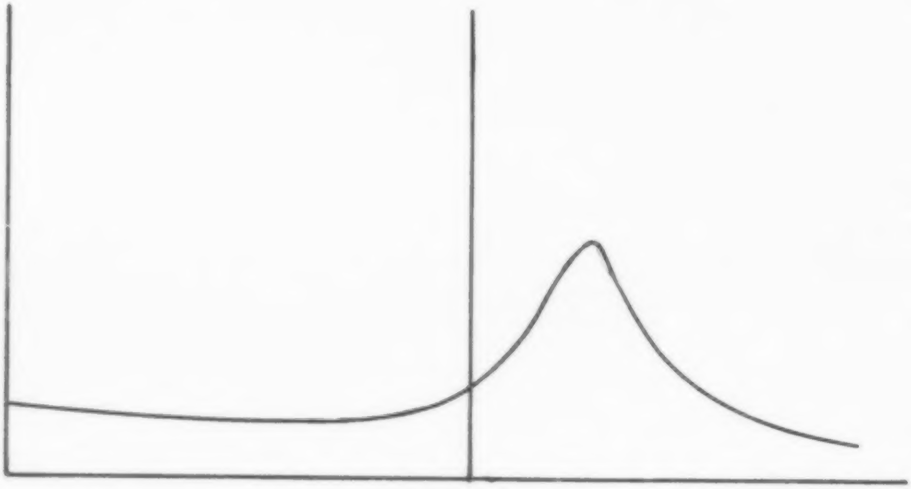


Figure 83 HYPOTHETICAL POLLUTANT PROFILES EXPECTED DURING OPERATION OF AIR BARRIER DURING PERIODS WITH VARIABLE RIVER CURRENTS AND WIND DIRECTIONS (SHEET 2 OF 2)

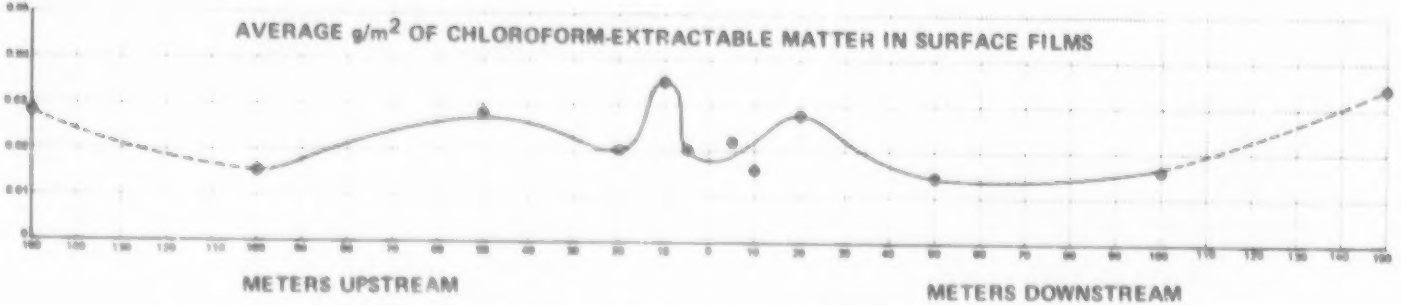


Figure 84 AVERAGE SURFACE FILM CONCENTRATIONS IN VICINITY OF AIR BARRIER OVER 10 DAYS OF CONTINUOUS OPERATION IN 1970

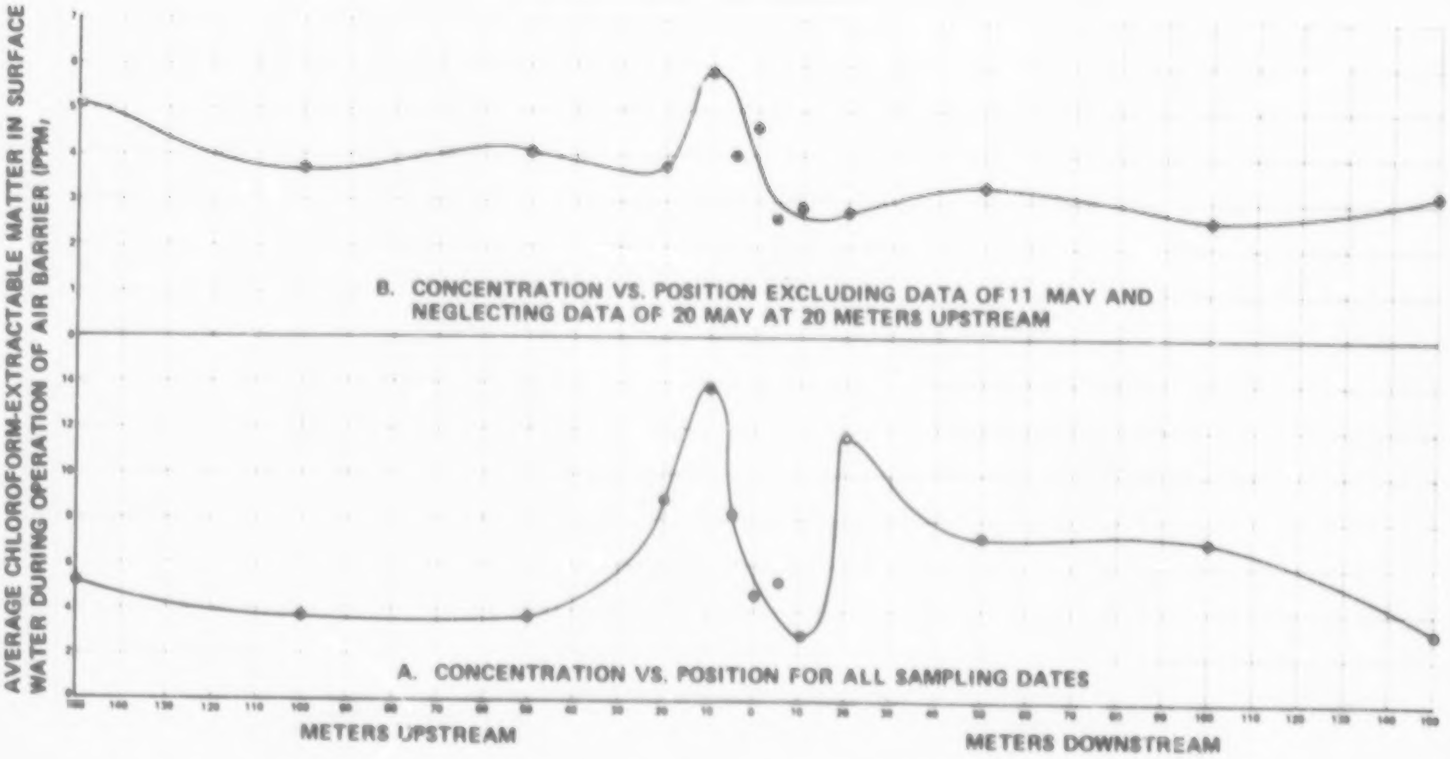


Figure 85 AVERAGE SURFACE WATER CONCENTRATIONS OF OILY POLLUTANTS IN VICINITY OF AIR BARRIER DURING 10 DAYS OF CONTINUOUS OPERATION IN 1970

arising from the condition just described as (3) and profiled on Figure 83 as condition (3); that is, this represents a situation where the wind is basically opposing the river current and the average water velocity contribution to the pollutant movement was apparently just balanced between current and wind. It is known that the Buffalo River flows generally westward, even though at a sluggish rate, and over the sampling period described here the prevailing winds over the river surface were southwesterly at about 12 mph. It will be noted in Figures 84 and 85 that the general patterns in both profiles are very similar; that is, the concentration of pollutants peaks in the identical position in the averages of results from the use of both sampling schemes. The apparent lack of correlation noted in the collected profiles presented in Figures 80 and 81, in apparent contradiction to the harmony and similarity achieved in the averages, has to do primarily with the great variability noted over this ten-day sampling period in the rainfall (and therefore the river flow rate) and in the wind directions.

In Figure 85, profile A represents the concentration vs. position profile for all data on all sampling dates, whereas trace B shows a somewhat idealized profile of the surface burden of chloroform extractable material produced by selectively rejecting certain of the data points. For example, in Figure 85B all of the May 11 data are omitted since they are higher than all of the other data accumulated by nearly a factor of 10. In addition, the one anomolously high point found 20 meters upstream of the air barrier on May 20 is omitted since it, too, appears to be an extraordinarily high value. The resultant profile shows that the air barrier concentrates the majority of pollutants, over the average, in the surface water approximately 10 meters upstream of the air curtain itself. Finally, in almost complete concurrence with the expected stream profiles predicted from knowledge of current flow and wind direction, the individual pollutant profiles in the collected surface films and in the immediately subjacent surface water are given in Figures 86 and 87. It will be noted that the profiles actually determined for each of the meteorological conditions and river flows annotated in these figures for the individual sampling dates, confirms almost perfectly the theoretical expectations for the performance of the air barrier. It should be noted that the mean flows on these figures were obtained from U.S.G.S. rating charts and from calculations of the cooling water throughputs from the major industries upstream. These mean flows are expressed as net river discharge through Sampling Site 10, and were noted to be constant between Sampling Site 10 upstream of the air barrier and Sampling Site 12, where the river discharged into Lake Erie.

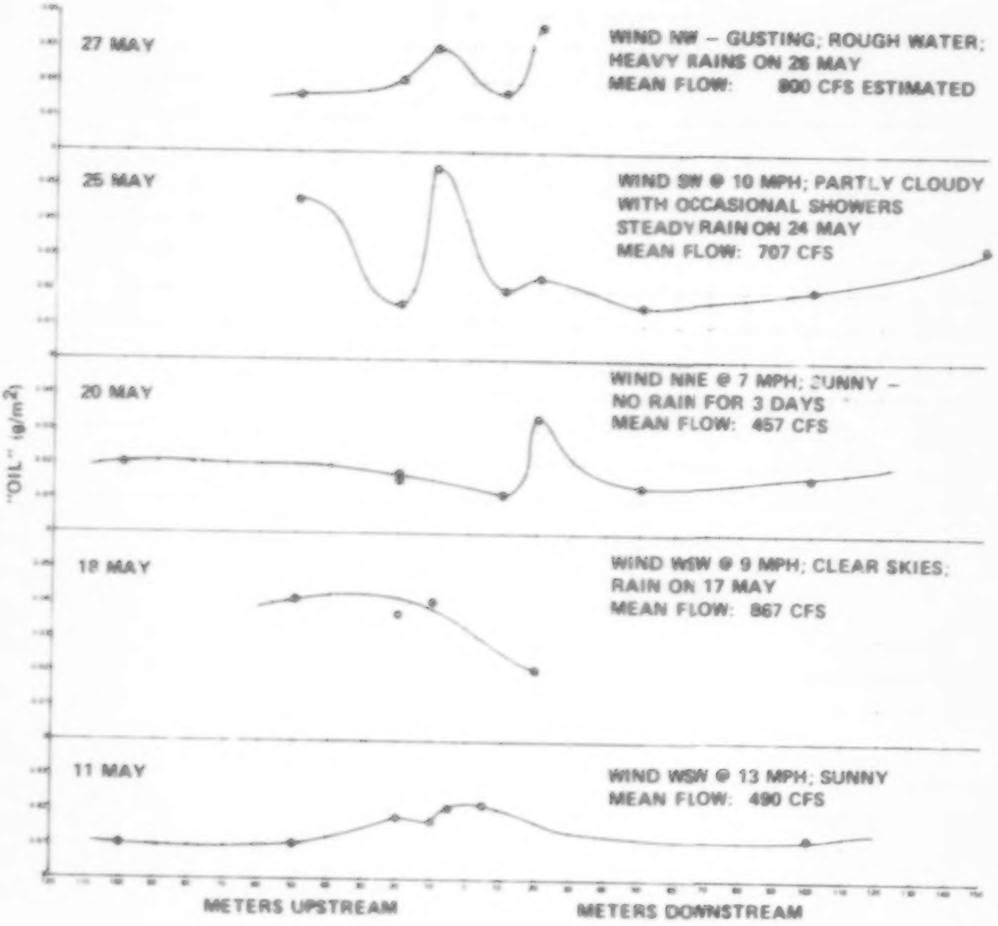


Figure 86 INDIVIDUAL POLLUTANT PROFILES FROM AIR BARRIER SURFACE-ACTIVE HOOP SAMPLES ON 5 SEPARATE DATES IN 1970

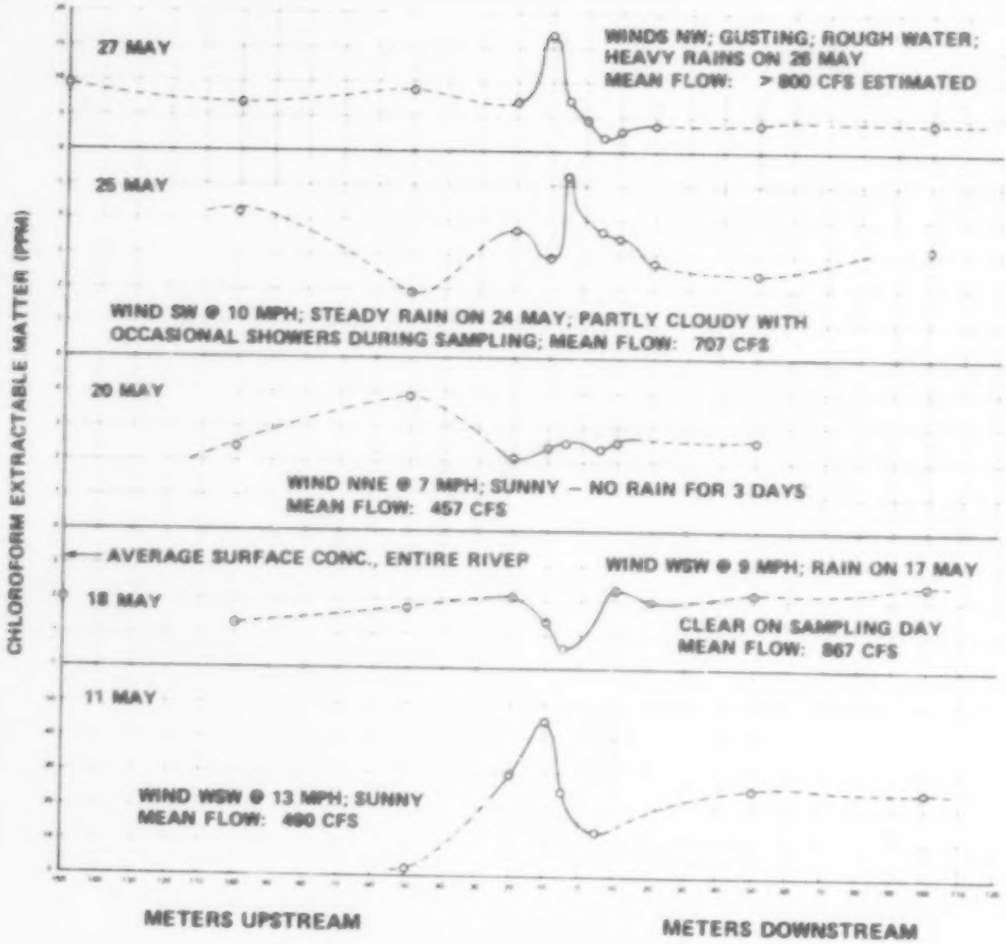


Figure 87 INDIVIDUAL POLLUTANT PROFILES FROM AIR BARRIER SURFACE SCREEN SAMPLES ON 5 SEPARATE DATES IN 1970

SAMPLING AND IDENTIFICATION IN SUPPORT OF THE EVALUATION OF AN INVERTED SIPHON SEWER AS AN OIL TRAP

This phase of the sampling and identification program had two major tasks: (1) to quantify the efficiency of the inverted siphon design as a trap for (a) surface oils and (b) bulk oils; (2) to identify, by providing analytical instrumental "fingerprints," the components of the oil pollutants and to indicate their most likely sources. The conclusions drawn from this sampling and analytical work, and documented in this section are:

1) The inverted siphon sanitary sewer design is nearly 100% effective for skimming of surface oils. This includes both surface oils that are constantly inputted, including such types as cooking oils and greases, and the adventitious large spills of petroleum oils that occur along an interceptor sewer line, from gas stations, railroad refueling operations, and other commercial sources.

2) The inverted siphon sewer design is nearly 0% efficient for bulk emulsified oils, almost all of which are very highly oxygenated.

3) The oils entering and trapped in the inverted siphon sanitary sewer interceptor, studied during this program, divided about 30% of biological origin and about 70% of petroleum origin. Specifically, the petroleum-based fuels were diagnosed as being essentially identical to No. 2 Fuel Oil on the basis of identical infrared spectra and gas chromatograms. No. 2 Fuel Oil was routinely used in railroad refueling operations in a major terminal adjacent to the inverted sewer section under study. Such oils were found, by a separate sampling, to be entering the sewer line from an oil sump overflow in the railroad terminal.

4) The majority of oils collected in 15 foot deep columns in the central sections of the inverted siphon sanitary sewer must have come to that section as floating oils in large spills in order to be consistent with the efficiency of the collection process noted and with the gas chromatographic analyses of the accumulated manhole contents. The inverted siphon section did not contribute significantly to emulsifying oils into the bulk phase from their original location as surface films.

Thus, the inverted siphon sewer provides an admirable mechanism for the trapping of and collecting of accidental or surreptitious oil spills into sewer lines. It is further an admirable mechanism for preventing efflux of such pollutants to either sewage treatment plants or as overflows into industrial watercourses. As a secondary feature, such inverted siphon sewers also effectively collect most other small floating objects. The instant example showed gross collections of floating vegetables and rubber products which had entered the sewer line upstream.

GENERAL OVERVIEW OF THE SITUATION

Using automated equipment described in another topical report of the Buffalo River Project (Reference 3), it was estimated during the 1969 and 1970 sampling seasons that the oil accumulations (to nearly 15' depths in two central manholes of the inverted siphon sewer section) ranged around approximately 1000 gallons per month total oil collection. It was further noted that the rate of increase could be correlated with the net rainfall received and discharged as runoff into the sewer lines. Therefore, it is reasoned that the inrushing rain water carried with it trapped or pooled oil residues from various stagnant locations along the sewer lines and interceptors.

Figure 88 is a sketch of the inverted siphon sanitary sewer interceptor discussed in this report and which received close examination during the spring, summer and fall of 1969 and again during the spring, summer and fall of 1970. Access to the inverted siphon section was quite direct from a series of manholes, the central four of which are labelled in Figure 88. The various surface and subsurface phases flowing through or accumulated in the upright siphon sections in this sanitary sewer interceptor are labelled on Figure 88 as identified by the combination of sampling and analytical techniques described earlier in this report. The mainstays of the sampling and analysis program were the prism dip technique for surface oils, the chloroform-extraction technique for bulk oils, and analysis by internal reflection and transmission infrared spectroscopy and gas chromatography.

Figure 89 illustrates a typical sequence of infrared spectra characterizing the surface material found in manholes No. 1 through No. 4 during the 1969 sampling season. The top trace in this figure shows the diagnostic spectrum of the input surface layers to the actual siphon section as determined from prism dip samples taken at manhole No. 1. This spectrum largely represents products of biological origin with the predominance of fatty materials (for example, triglycerides) and proteins. A simple mixture of cooking greases and proteins (for example, egg whites or vegetable extracts) would match this spectrum almost exactly. The second spectrum from the top in Figure 89 typifies the surface of the very deep column of accumulated oils and greases in manhole No. 2 which most often included some very large vegetable fragments as well. In this spectral trace, one will note that a shift has occurred in one of the major infrared absorption bands from the position representing esters, as in the uppermost trace in Figure 89, to a position more representative of fatty acid by-products from degradation of the biological esters (note the sharp spike in the region around 1700 cm^{-1}). This shift is a strong indication that active bacterial degradation of the materials entering the siphon section was taking place throughout the spring, summer and fall months and the odoriferous gases emitted from these manholes further attested to this fact. The third trace from the top in Figure 89 represents the surface layers of the second vertical column (in manhole No. 3)

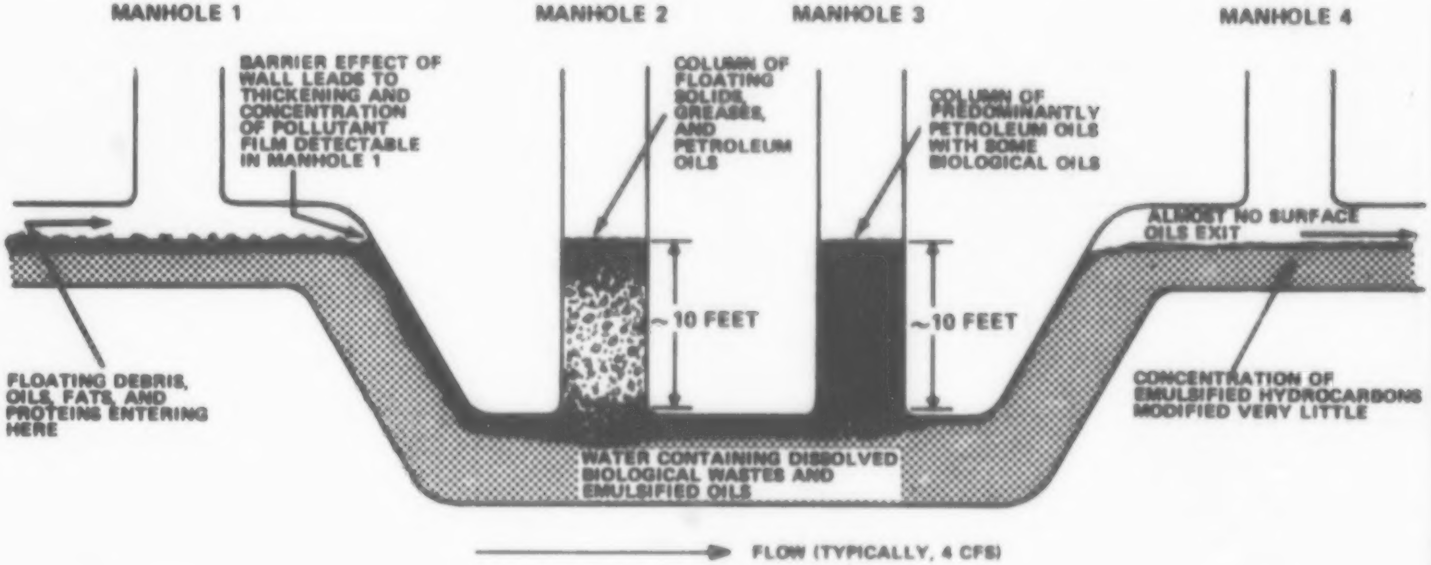

MANHOLE 1
MANHOLE 2
MANHOLE 3
MANHOLE 4
BARRIER EFFECT OF WALL LEADS TO THICKENING AND CONCENTRATION OF POLLUTANT FILM DETECTABLE IN MANHOLE 1
COLUMN OF FLOATING SOLIDS, GREASES, AND PETROLEUM OILS
COLUMN OF PREDOMINANTLY PETROLEUM OILS WITH SOME BIOLOGICAL OILS
ALMOST NO SURFACE OILS EXIT
~10 FEET
~10 FEET
FLOATING DEBRIS, OILS, FATS, AND PROTEINS ENTERING HERE
CONCENTRATION OF EMULSIFIED HYDROCARBONS MODIFIED VERY LITTLE
WATER CONTAINING DISSOLVED BIOLOGICAL WASTES AND EMULSIFIED OILS
FLOW (TYPICALLY, 4 CFS)

Figure 88 INVERTED SIPHON SECTION OF SANITARY SEWER AND ITS FUNCTION AS AN OIL TRAP FOR SURFACE—LOCALIZED POLLUTANTS

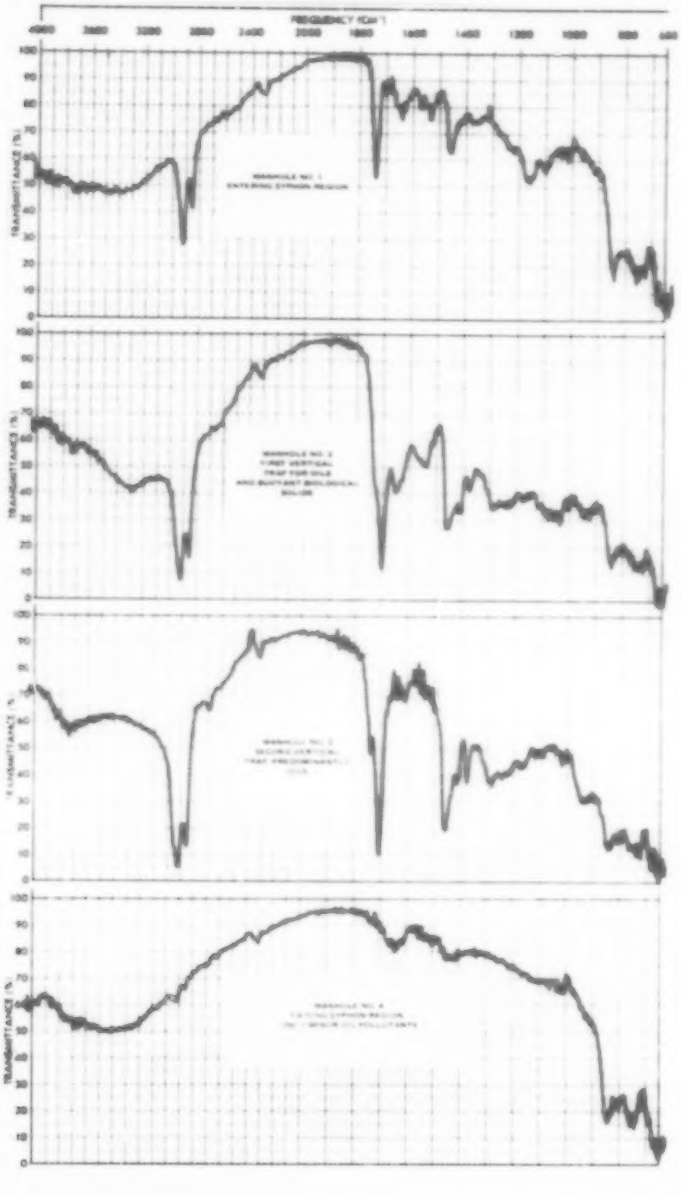


Figure 89 CHARACTERISTIC INFRARED SPECTRA OF POTENTIAL RIVER POLLUTANTS ENTERING, TRAPPED IN, AND EXITING INVERTED SIPHON SANITARY SEWER

of the accumulated "skimmings" from the flowing stream. Comparison of this spectrum with that from manhole No.2 shows that most of the proteinaceous material (typified by absorption bands near 3300, 1650, and 1550 cm^{-1}) is well trapped in the first vertical section and does not enter this second manhole standpipe. Otherwise, the oily fraction was essentially identical in both columns. It should be pointed out that the very sharp central spike (in spectra for the vertical manholes No. 2 and No. 3) characterizing these columns of light oils is not typical of exclusively petroleum-based oils such as diesel fuels or other hydrocarbon fuels. Rather, a mix of such oils with biological products is indicated. It is significant to note that upstream of this sanitary sewer interceptor is a large municipal market place which prepares meats and vegetables for retail trade and provides inputs to the sanitary sewer line.

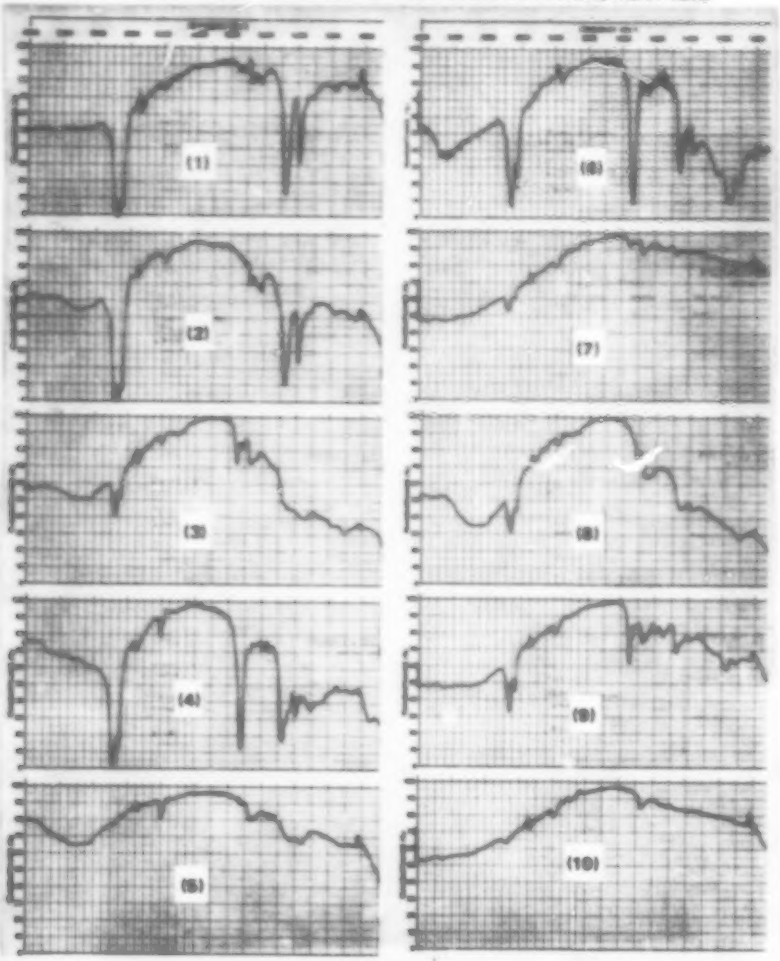
The final (lowermost) spectrum in Figure 89 is illustrative of the dramatic improvement in the surface quality of the effluent stream from the inverted siphon section. Almost all traces of surface oils, proteins, indeed any surface debris, are completely eliminated. This is indicated by the relative absence of large absorption spikes in the infrared trace. However, these data do not bear on the quality of the bulk liquid flowing below. The bulk sampling reported further in this section indicates that the efficiency of the siphon for trapping oil from the bulk liquid is markedly lower than the efficiency noted here for the skimming and trapping of surface oils.

Figure 90 presents two sequences of infrared spectra characterizing (a) potential oily pollutants of petroleum and biological origin with a likelihood of entering the sewer line feeding this inverted siphon section, (b) actual oily pollutants entering and collected in the inverted siphon section of the sewer, and (c) the surface quality of the skimmed water exiting the inverted siphon section of the sewer line. Here again, it can be readily seen from intercomparison of these various infrared spectral traces that the accumulated oil columns in the central manholes of the inverted siphon section are best described as mixed oils of petroleum origin and of biological origin (mostly greases). The efficiency of the inverted siphon section as a skimmer or "cleanser" for these surface oils is dramatic. All samples included in Figure 90 were collected by the prism dip technique during October and November of 1970.

EVALUATION OF THE INVERTED SIPHON SECTION OF THE SEWER AS AN OIL TRAP FOR POLLUTANTS EMULSIFIED OR SUSPENDED IN THE BULK WATERS

A sampling program to evaluate the efficiency of the inverted siphon for trapping bulk oil suspended in the water volume was begun in 1969 and completed during 1970. The inverted siphon section selected for analysis here was the same as already described. The results from the in-sewer remote monitoring program continuously indicated large amounts of oils periodically accumulated in the two innermost manholes. The question was then: "What is the origin of these very large amounts of

(1) OIL IN FLOTATION TRAP IN RAILROAD YARD; OCT. 1970
(2) MANHOLE IN LINE CONNECTING OIL SEPARATOR AND OIL SUMP IN RAILROAD YARD; OCT. 1970
(3) MANHOLE 1 INLET TO INVERTED SIPHON SEWER SECTION; OCT. 1970
(4) SURFACE OF 12-FOOT-DEEP OIL ACCUMULATION IN MANHOLE 3 OF INVERTED SIPHON SEWER SECTION; OCT. 1970
(5) MANHOLE 4 OUTFLOW FROM INVERTED SIPHON SEWER SECTION; OCT. 1970
(6) TYPICAL SPECTRUM OF "OIL" OF BIOLOGICAL ORIGIN (GREASES, FATS, VEGETABLES, SEWAGE); NOV. 1970
(7) FIRST MANHOLE UPSTREAM OF RAILROAD TERMINAL; NOV. 1970
(8) FIRST MANHOLE AFTER OIL SUMP IN RAILROAD YARD; NOV. 1970
(9) MANHOLE 1 INLET TO INVERTED SIPHON SEWER SECTION; NOV. 1970
(10) MANHOLE 4 OUTFLOW FROM INVERTED SIPHON SEWER SECTION; NOV. 1970



NOTE: ALL SAMPLES COLLECTED BY THE PRISM-DIP TECHNIQUE DURING OCTOBER AND NOVEMBER 1970.

Figure 90 TWO SEQUENCES OF INFRARED SPECTRA CHARACTERIZING (A) POTENTIAL OILY POLLUTANTS OF PETROLEUM AND BIOLOGICAL ORIGIN WITH LIKELIHOOD OF ENTERING SEWER LINE, (B) ACTUAL OILY POLLUTANTS ENTERING AND COLLECTED IN INVERTED SIPHON SECTION OF SEWER, AND (C) SURFACE QUALITY OF "SKIMMED" WATER EXITING INVERTED SIPHON SECTION OF SEWER

oil and could they have been derived from oils emulsified in the bulk?" The source of much of this oil had been traced earlier by the Buffalo Sewer Authority and the New York State Environmental Conservation Department to a railroad refueling installation nearby and this identification by source was confirmed by Cornell Aeronautical Laboratory analysts during the current program. During 1969, one extensive sampling period extended over a full week, night and day. Continuous results were obtained over the final five days of this seven-day period wherein the influent and effluent streams were sampled every 30 minutes at manholes No. 1 and No. 4, respectively. These samples were composited daily and analyzed for the total concentration of hexane-extractable materials and for the relative proportions of oils of biological and of petroleum origin. In addition, the central manholes (No. 2 and No. 3 in the siphon trap chamber) were sampled every day and at the beginning and the end of the program. The samples from these two manholes were taken at two-foot intervals from the top of the oil column to its junction with the flowing water many feet below and analyzed for total hexane-extractable materials only. The purpose of the latter sampling was to attempt to relate the inflow content and the outflow content to the change of net storage in the inverted siphon system. Hexane-extraction of the water samples was used in this investigation, since the laboratory program which determined chloroform-extraction to be superior had not been completed at the time.

Prior to initiation of the sampling program, the siphon manholes were completely freed from their initial accumulation of oils and solid burden. The flow volume through the inverted siphon section sewer was calculated by means of the Manning Equation which relates flow volume to the hydraulic properties of the channel. As an input to the Manning Equation, the flow depths in the inlet and outlet sections were recorded by a staff gauge.

During the entire course of this round-the-clock survey, the concentration of hexane-extractables of the influent stream averaged about 23 ppm. This is a value typical of the concentrations received routinely at the City of Buffalo Sewage Treatment Plant from all of the combined sewage influents. Approximately 80% of the extractable oily content of the influent stream was material of biological origin. It is apparent that the bulk waters flowing through the sewers do not carry a heavy enough oil flow to account for the gross accumulations noted in the inverted siphon section and, therefore, potential surface spills from industrial sources must be more carefully examined.

Results of the 1969 sampling program indicated, on the whole, that the inverted siphon was not effective at all for trapping emulsified materials. In five of seven of the composite samples, a small decrease ranging from 3 to 9 ppm was noted in the concentration of total extractable material between the influent and effluent streams. However, on two occasions this concentration was reversed. A net result was that, at best, the inverted siphon sewer was trapping 20% of the potential emulsified oily pollutants entering in the bulk water.

Figure 91 shows infrared spectra of the chloroform-extractable matter (chloroform extraction has been found to be more complete than hexane extraction) in the bulk water entering and exiting the inverted siphon section of the sanitary sewer. Inspection of these two spectra will show that they are essentially identical and that transit of the bulk water through the inverted siphon sewer did not, in any significant way, modify either the oil properties or the oil content.

CHARACTERIZATION OF THE OIL POLLUTANTS ACCUMULATED IN THE VERTICAL COLUMNS IN AN INVERTED SIPHON SECTION OF A SANITARY SEWER

Collections were made of the deep oil accumulations in manholes No. 2 and No. 3, in the oil trapping section of the inverted siphon sewer, in October of 1970. Manhole No. 2 was sampled at the 1/2 meter depth from its surface and at the 2 meter depth from it surface. Sampling at greater depths was frustrated by large amounts of debris and encrusted material. Manhole No. 3 was sampled at the 1/2 meter depth from its surface, at the 2 meter depth and at the 4 meter depth. These samples were then subjected to analysis by gas chromatography and by infrared spectroscopy. During the gas chromatographic analysis, the following conditions were used which should be recorded. The column was a 10% silicone column labelled UCW9880, 6 feet in length. A dual flame ionization detector was used at 300°C. The injection port temperature was 260°C. The column oven was programmed from 100°C at 15°C per minute to 250°C, kept isothermally. A sample volume for injection was 1.5 microliter plus or minus 0.2 microliter. During a series of chromatographic analyses of various hydrocarbon and fuel standards, and of the sewer samples themselves, the instrument attenuation was varied from 1 to 16 and the range setting was 10^4.

The following samples were analyzed: (a) hydrocarbon standards of C_6 through C_{16}, which were normal hydrocarbons to establish the nominal boiling point range (the source of these standards was the Hewlett-Packard Corporation); (b) standard diesel fuel provided by a local oil refinery; (c) No. 2 Fuel Oil which was also a standard provided from an oil refinery and known to have a slightly higher boiling point range than the diesel fuel cut; (d) South Louisiana Crude Oil; (e) Paraffin oil containing predominantly high boiling hydrocarbons with chain lengths greater than C_{16}; (f) and all of the oil samples from the inverted siphon sewer.

Figure 92 presents gas chromatograms characterizing the oily pollutants accumulated at various levels in manholes No. 2 and No. 3 of the inverted siphon sewer. The results are best seen by inspection of these chromatograms, but briefly they are as follows: In manhole No. 2 at the 1/2 meter depth, the chromatogram contained two peaks indicating low boiling components, but the balance was nearly identical to the chromatogram for No. 2 Fuel Oil. At the 2 meter depth in this same manhole, the chromatogram was nearly identical to that of the 1/2 meter depth sample but with the absence of the low-boiling compounds, thereby indicating that

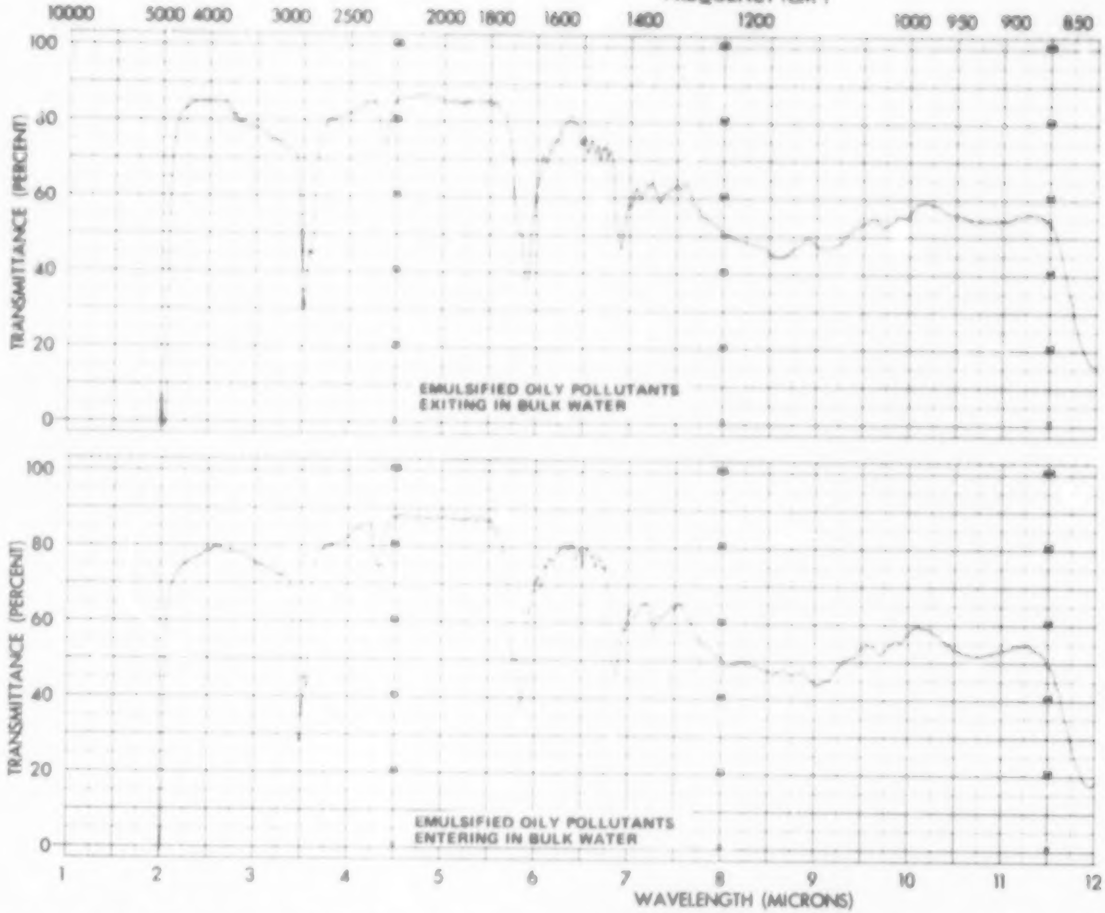
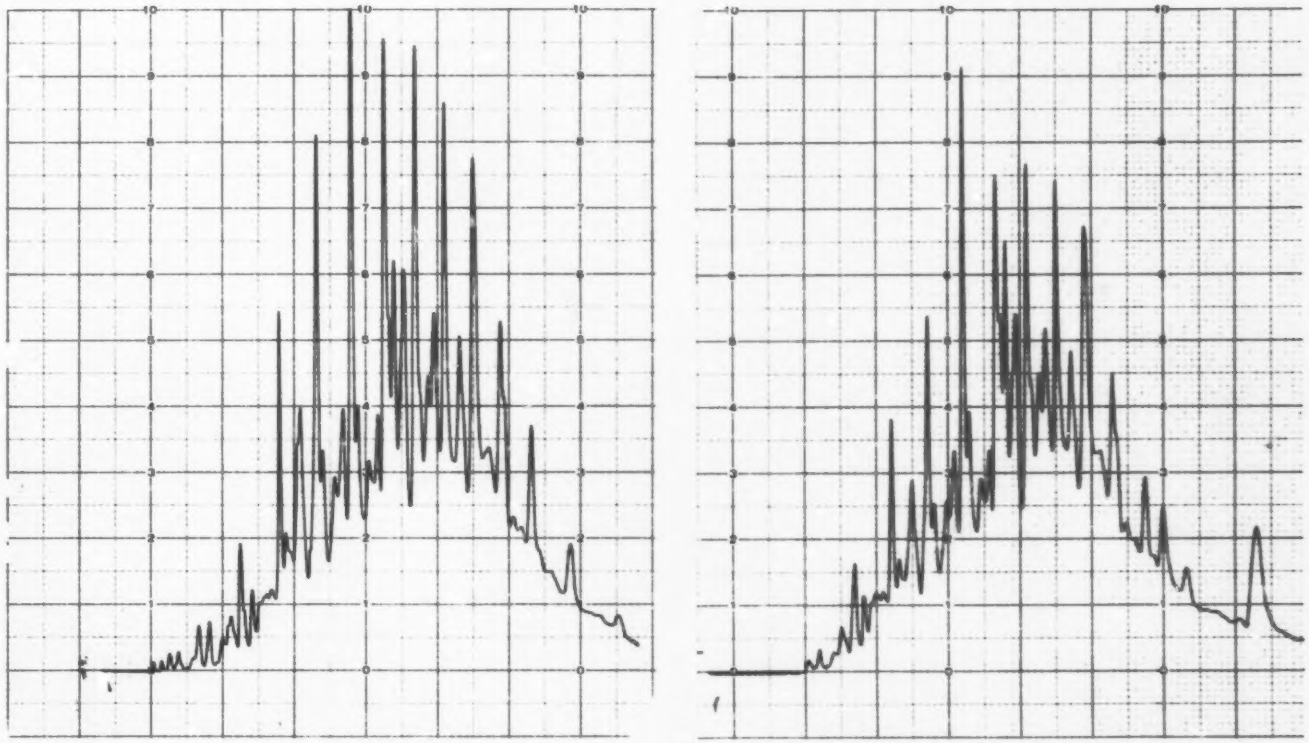


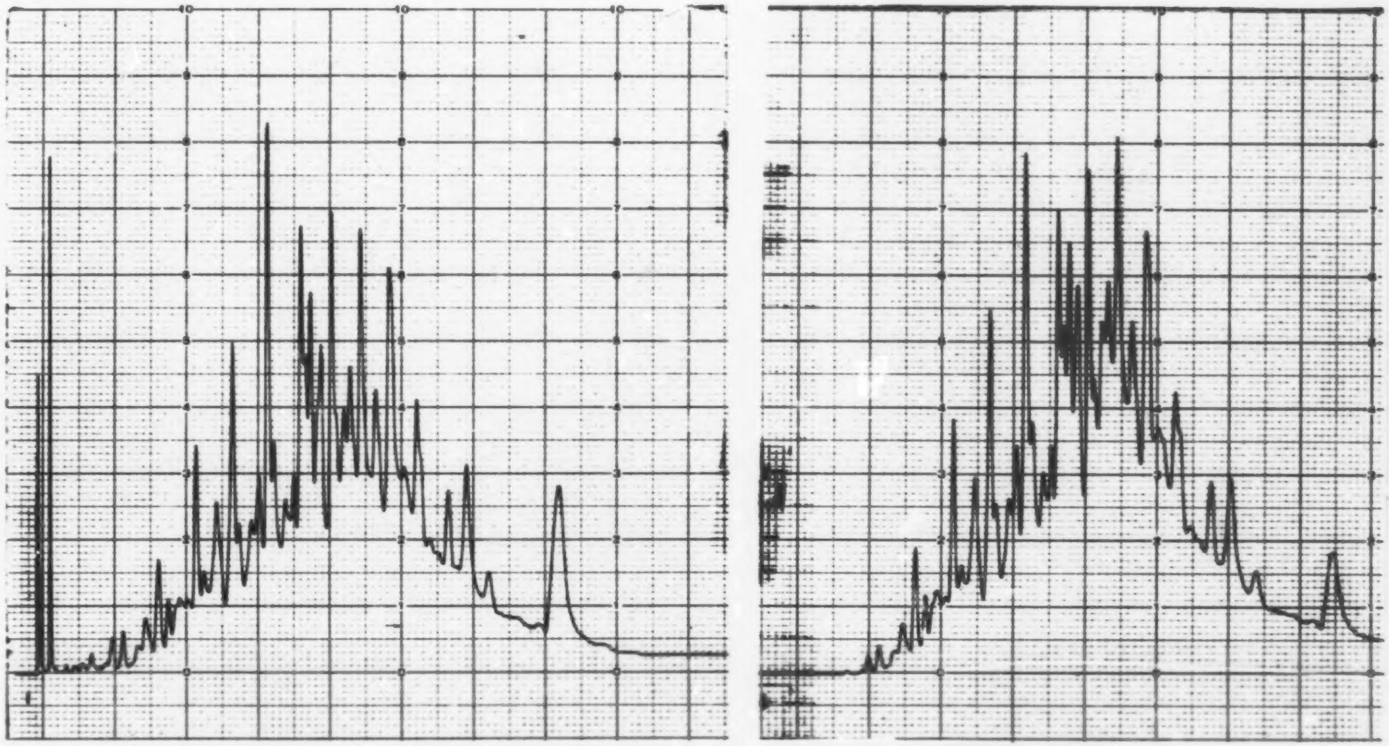
Figure 91 INFRARED SPECTRA OF CHLOROFORM-EXTRACTABLE MATTER IN BULK WATER ENTERING AND EXITING INVERTED SIPHON SECTION OF SANITARY SEWER



NO. 2 FUEL OIL

MANHOLE 3 - DEPTH OF 1/2 METER

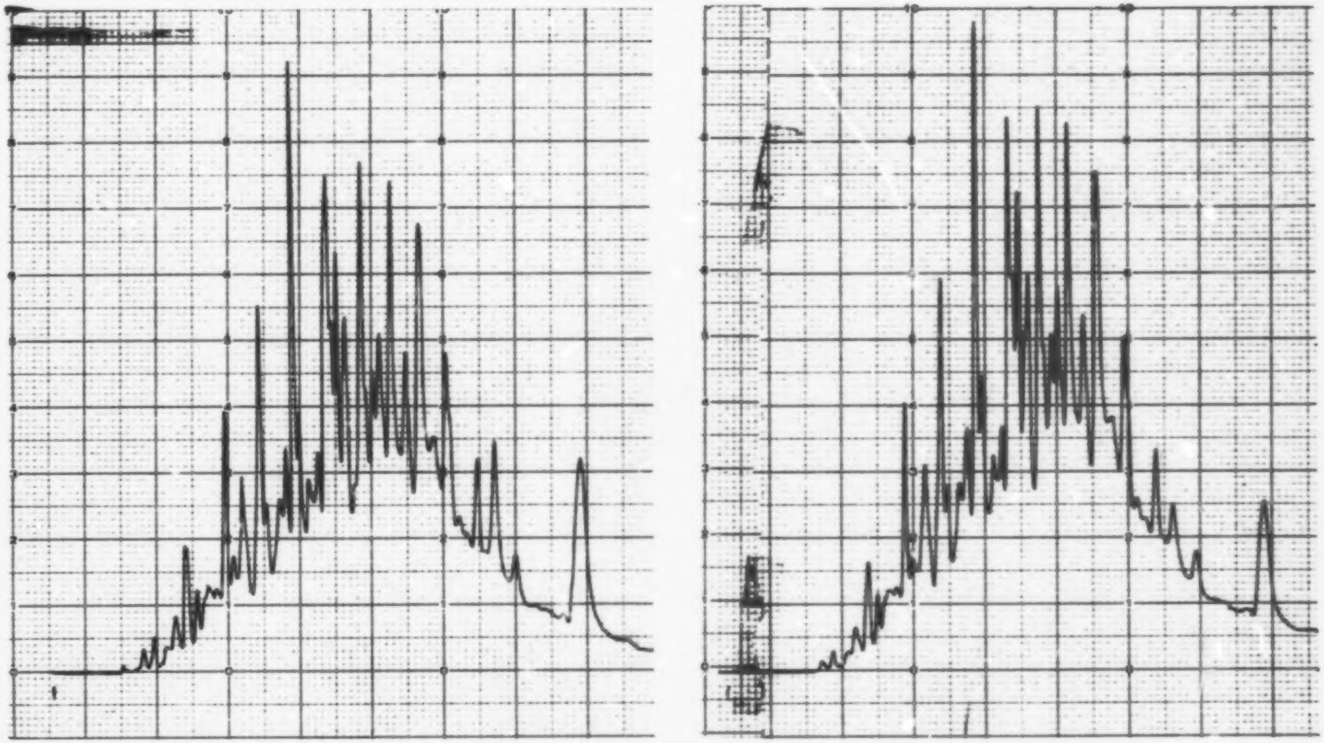
Figure 92 GAS CHROMATOGRAMS CHARACTERIZING THE OILY POLLUTANTS ACCUMULATED AT VARIOUS LEVELS IN MANHOLES 2 AND 3 OF THE INVERTED SIPHON SEWER (SHEET 1 OF 3)



MANHOLE 2 - DEPTH OF 1/2 METER

MANHOLE 3 - DEPTH OF 2 METERS

Figure 92 GAS CHROMATOGRAMS CHARACTERIZING THE OILY POLLUTANTS ACCUMULATED AT VARIOUS LEVELS IN MANHOLES 2 AND 3 OF THE INVERTED SIPHON SEWER (SHEET 2 OF 3)



MANHOLE 2 - DEPTH OF 2 METERS

MANHOLE 3 – DEPTH OF 4 METERS

Figure 92 GAS CHROMATOGRAMS CHARACTERIZING THE OILY POLLUTANTS ACCUMULATED AT VARIOUS LEVELS IN MANHOLES 2 AND 3 OF THE INVERTED SIPHON SEWER (SHEET 3 OF 3)

these low-boilers were of lower density and thus preferentially accumulated at the top. These components were very likely being rapidly lost to the atmosphere by evaporation.

In manhole No. 3, the 1/2 meter depth sample chromatographed to be nearly identical to No. 2 Fuel Oil as did the samples from the 2 meter depth and 4 meter depth. Using attenuation data recorded during the operations of the chromatograph on the various hydrocarbon oil standards, we were able to estimate the approximate concentrations of No. 2 Fuel Oil in each of these samples. Assumptions made in this estimate were (1) that the sample sizes were constant, and (2) that the chromatogram of the No. 2 Fuel Oil standard represented 100% of the injected sample volume.

In manhole No. 2 at the 1/2 meter depth, approximately 70% of the volume of the sample was represented by No. 2 Fuel Oil and at the 2 meter depth a similar result was obtained. In manhole No. 3 (the second manhole encountered by floating oils entering the inverted siphon section of the sewer) at the 1/2 meter depth, again approximately 70% of the volume can be accounted for as No. 2 Fuel Oil. At the 2 meter depth, however, the chromatogram indicated essentially 100% No. 2 Fuel Oil whereas at the 4 meter depth, the volume fraction was again down to about 70%.

Thus, one can see that the biological components represented at the most 30% of the oils entering and trapped in the inverted siphon section of the sanitary sewer and that these were preferentially accumulated in manhole No. 2 first. When manhole No. 2 was full, they then entered manhole No. 3. The large volume of petroleum oil representing the mid-depths in manhole No. 3 most likely resulted from an accidental or surreptitious petroleum discharge into the sewer line from the nearby railroad yard. Later gas chromatograms of samples collected directly from the railroad terminal (from the storage pump and from the oil sump and separator) showed that the chromatograms of that material were identical to our No. 2 Fuel Oil standard and to the material found accumulated in the inverted siphon sewer section.

Figure 93 is a collection of infrared spectra characterizing the oily pollutants accumulated at the various levels in manholes No. 2 and No. 3 of the inverted siphon sewer. Comparing the traces from manhole No. 2 with those from manhole No. 3, it will be noted that a difference exists in the relative intensities of the absorption bands correlating with (a) straight chain hydrocarbons of petroleum origin and (b) groups in the highly oxygenated oils of biological origin. When the ratios of the hydrocarbon and ester peaks were obtained, manhole No. 2 showed ratios of 1.6 at the half meter depth and of 1.7 at the 2 meter depth while manhole No. 3 showed ratios of 2.3, 2.1, and 2.4 at the half, 2, and 4 meter depths respectively. In this comparison, a low ratio indicates more carbonyl groups. Therefore, the oil in manhole No. 2 is (or has mixed with it) more oxygenated material than is the oil making up the volume in manhole No. 3. These results confirm the conclusions from the gas chromatography just discussed.

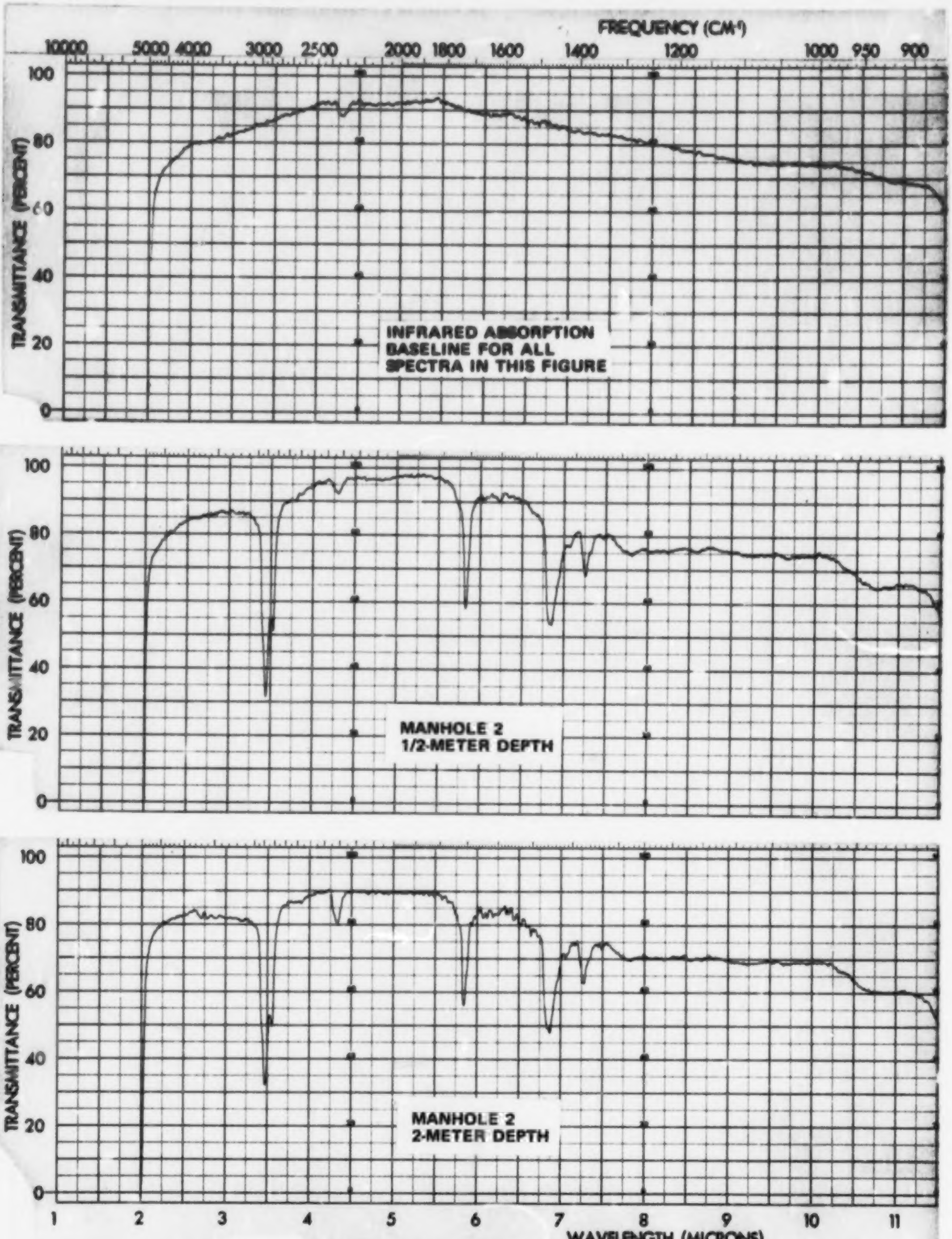


Figure 93 INFRARED SPECTRA CHARACTERIZING THE OILY POLLUTANTS IN MANHOLES 2 AND 3 OF THE INVERTED SIPHON SEWER (SHEET 1 OF 2)

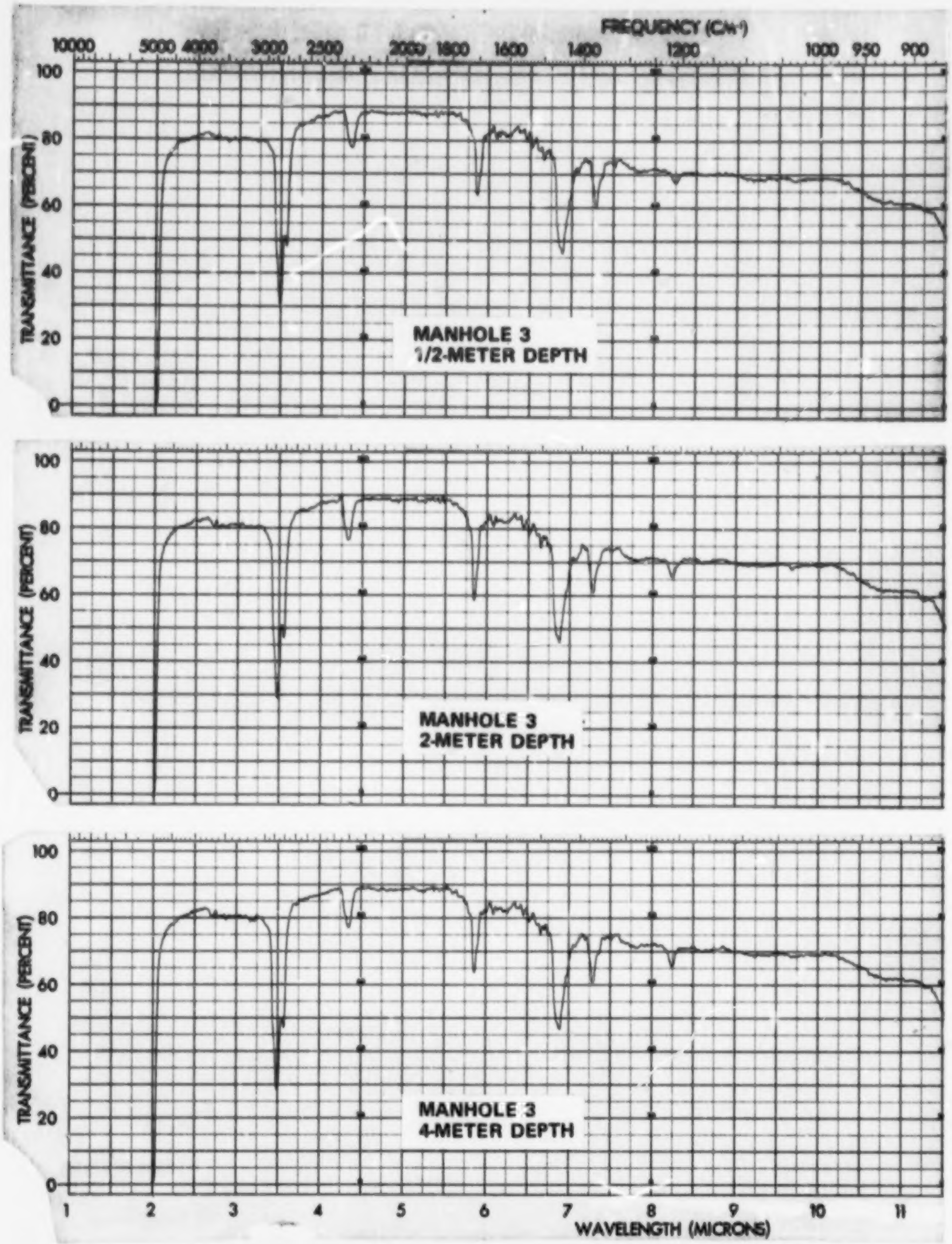
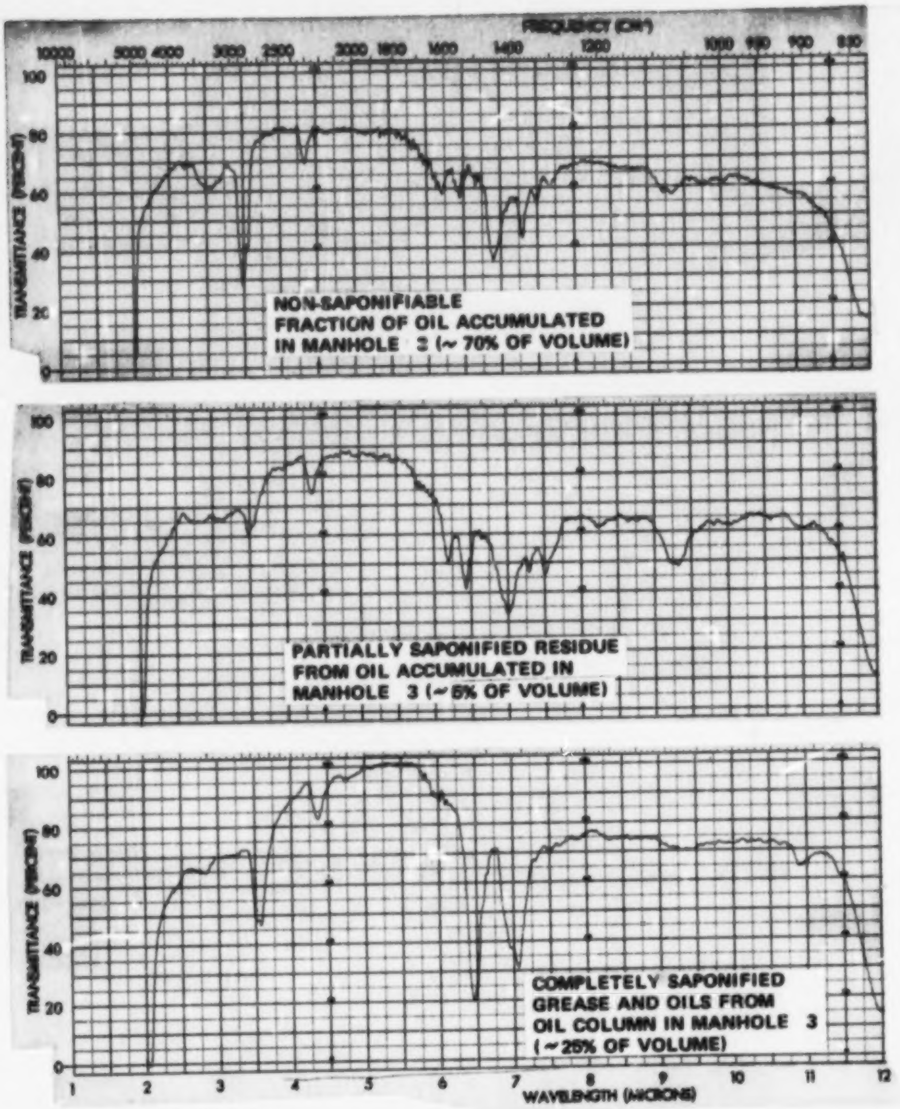


Figure 93 INFRARED SPECTRA CHARACTERIZING THE OILY POLLUTANTS IN MANHOLES 2 AND 3 OF THE INVERTED SIPHON SEWER (SHEET 2 OF 2)

Intercomparing the infrared spectra of the oils from the various depths in each manhole, no substantial differences are seen. Thus, there has been a good solubilization or admixing of the biological fractions with the petroleum oil fractions in each vertical column. As yet a final check on the separability of the oils that accumulated in these two vertical standpipes, typical chemical saponifications were undertaken on material from each of the manholes. As an illustration, Figure 94 shows infrared spectra of variously saponifiable fractions of the oil accumulated in manhole No. 3 of the inverted siphon sewer. These traces illustrate the simultaneous presence of oils of both biological and petroleum origin. The procedure for obtaining the traces in Figure 94 was as follows. First, some ethyl alcohol was saturated with sodium hydroxide and then the base-saturated alcohol added to a sample of oil taken directly from the No. 3 manhole. In order to separate the saponified solids from the mixed sample, centrifugation for five minutes at 1200 rpm was carried out. The uppermost infrared scan in Figure 94 is of the supernatant non-saponifiable oil fraction of petroleum origin in this sample and represented some 70% of the volume. The central scan in Figure 94 was produced by extraction of this supernate with acetone, alcohol, and chloroform to leave a solid white residue of tiny solid matter that had not been efficiently separated from the supernate during centrifugation. This represents material only partially saponified, or partially solidified by the reaction with sodium hydroxide. The lowermost spectrum was produced from the solids as filtered from the bottom slurry collected during the centrifugation and washed with acetone, alcohol, and chloroform. This material accounted for approximately 25% of the total volume of the oils when examined by this chemical technique.

MASS BALANCE CALCULATIONS FOR THE INVERTED SIPHON SEWER

During October of 1970, a number of samples were taken upstream and downstream of the inverted siphon sewer in order to estimate the contributions to the oil build-up from the floating films and from the emulsified oil, respectively. The bulk water entering the inverted siphon section, as sampled through manhole No. 1, was flowing (on the sample day) at 1.23 ft/sec and with a water depth of 14 inches. Net discharge through the pipe was calculated to be 3.73 ft^3/sec. Sampled through manhole No. 4, downstream of the inverted siphon oil traps, the flow was discovered to be 1.04 ft/sec with the water depth of 15.5 inches and the discharge rate of 3.86 ft^3/sec. Thus the average discharge through the inverted siphon section of the sewer was about 3.8 ft^3/sec. The calculations of discharge were actually made assuming a circular cross-section of the pipe, then calculating the area occupied by a segment whose chord was appropriate to the depth actually measured, followed by calculating from the geometrical cross-sectional area the actual discharge through the section in cubic feet per second. Based upon calibration data for the prism dip technique presented elsewhere in this report, the average entering surface film thickness of oils was taken as 0.05 micrometers or 500 angstroms. Given this film



NON-SAPONIFIABLE
FRACTION OF OIL ACCUMULATED
IN MANHOLE 3 (~ 70% OF VOLUME)

PARTIALLY SAPONIFIED RESIDUE
FROM OIL ACCUMULATED IN
MANHOLE 3 (~ 5% OF VOLUME)

COMPLETELY SAPONIFIED
GREASE AND OILS FROM
OIL COLUMN IN MANHOLE 3
(~ 25% OF VOLUME)

Figure 94 INFRARED SPECTRA OF VARIOUSLY SAPONIFIABLE FRACTIONS OF THE OIL ACCUMULATED IN MANHOLE 3 OF THE INVERTED SIPHON SEWER, ILLUSTRATING THE SIMULTANEOUS PRESENCE OF OILS OF BOTH BIOLOGICAL AND PETROLEUM ORIGIN

thickness, and velocity and geometry of the flow in the pipe, the quantity of surface oil flowing into the inverted siphon section was calculated. With these values and the assumptions already noted, it was determined that approximately 1/2 gallon per day of biological oils (which the infrared spectra indicated with certainty were the predominant components floating on the inflow stream), or over a monthly period some 15 gallons per month, should be found to accumulate in the inverted siphon section (notably in manhole No. 2) if no other sources existed.

In the bulk water samples taken on the inflow and the outflow sides of the inverted siphon, the inflow water concentration was found to be 15.6 ppm extractable oils and the outflow had only a slightly lower value of 15.1 ppm extractable organics. Thus, carrying out a very straightforward calculation, it could be determined that between 1100 and 1200 gallons of oil were available per month in the inflow bulk water. Since the efficiency of siphon-trapping was so poor for these emulsified or suspended organic pollutants, the actual accumulation that the oils in the bulk water could account for in the inverted siphon section would amount to only 30 gallons per month. Thus, the 15 gallons per month from the surface films and the 30 gallons per month from the sewer waters in their natural "sewage" state falls far below the actually recorded 1000 gallon per month of oil-buildup in the inverted siphon section of the sewer line.

Taking the combined data presented here, that some 70% of the actual accumulated mass in the vertical standpipes (that is in manholes No. 2 and No. 3) was of petroleum origin and matched, by most analytical criteria, the No. 2 Fuel Oil used regularly adjacent to this inverted sewer line at a railroad refueling terminal, the conclusion seems inescapable that adventitous spills of this material were finding their way into the sewer at times that went unnoticed by sampling and other investigators during the course of this Buffalo River project. It is also certain, taking into account the relative efficiencies of trapping of the bulk oils vs. the surface oil films, that the oils accumulated in the vertical manholes must have entered that section as floating oils in very large amounts over very short periods of time.

Documentation of these findings was provided to the Buffalo Sewer Authority and to the New York State Department of Environmental Conservation. Based on these data and on observations of State personnel, an enforcement proceeding is now in progress.

SAMPLING AND IDENTIFICATION IN SUPPORT OF THE SKIMMER EVALUATION TASK

Previous sections of this report have demonstrated that in the Buffalo River, which may be taken as an example of a typical industrial watercourse in the Northeastern United States, the pollutant oils are often found widely dispersed over the river surface, are more often than not weathered and substantially oxidized, and are often pocketed in various lagoons, under piers, or in boat slips along the river shoreline. Further, there is a very large burden of shoreline deposits of weather-congealed oils and greases and an oil deposit of unknown quantity in the bottom sediments. The major carrier of oily pollutants from the industrial watercourse into its receiving body of water is the bulk water itself. In order for any fixed boom and skimmer operation to be effective in a control program on an industrial waterway such as the Buffalo River, it will be necessary to select techniques to control and concentrate and guide the surface oils to the skimmer location, to scavenge the oils from the shorelines and the sediments, and to bring emulsified oil suspended in the bulk water to the surface for subsequent damming and skimming. The previous section of this report on the use of an air barrier to contain surface oil gave some suggestions that the rising air bubbles could serve a secondary purpose of bringing emulsified or dissolved oils to the surface by air flotation mechanisms. The use of such a technique will never be highly efficient since air flotation technology applied to industrial, oily wastes have been reported to be effective in reducing oily concentrations of waste waters only to the 25 to 100 ppm contamination level. It will be recalled from earlier sections of this report that the oil concentrations in the Buffalo River bulk water normally do not exceed 25 ppm.

Thus, the oil most likely to be readily removed from an industrial watercourse is that immediately at the water surface and potentially amenable to skimming. However, even this type oil is difficult to collect efficiently because of the strong influence of meteorological and flow conditions on its presence, concentration and handling qualities. As a single example of the very large variability in the surface oil available for skimming near a permanent boom location, the following data are relevant.

During September of 1970, samples were taken upstream and downstream of a fixed surface boom at 10:30 in the morning and again at 1:30 in the afternoon. The sampling method was the surface screen technique described in earlier sections of this report. In the 10:30 A.M. sample, the upstream concentration of skimmable oil was found to be only 1.8 ppm and the concentration downstream was 17.8 ppm. At the 1:30 sampling time, the upstream concentration had increased markedly to 28.8 ppm and ten-fold increase was noted in the downstream collection of 187.2 ppm. These figures are also indicative of the major influence of the prevailing upriver wind on the oil concentration in the surface waters of the Buffalo River. They show that the upriver oil concentration collected at the boom was substantially less than that collected from the downriver waters, which in principle would have been expected to be flowing towards the river mouth.

The large increase in oil concentration measured in the afternoon of this particular sampling day could be correlated directly with the observed increase in wind speed from the morning to the afternoon which resulted in greater quantities of oil blown upstream to the boom. This indicates that larger quantities of surface oil can be made available for skimming if care can be taken to have the wind working with, rather than against, the operator.

From data presented earlier in this report, it is obvious that the preponderance of oil contained in the discharge of the Buffalo River is suspended throughout its bulk rather than floating on the surface. However, it is not self-evident that a boom and skimmer operation must fail in an industrial watercourse such as the Buffalo River because other observations recorded in this report have shown that occasionally very thick and extensive surface oil slicks occur at quiescent shorelines and meanders and bends in the upstream sectors of the river. There, portable skimmers assisted by chemical scavenging agents would allow effective collection of very large amounts of such oil.

Over the 1969 and 1970 sampling seasons, various types of oil skimming equipment were considered and investigated. Most of the equipment initially considered for oil retrieval did not prove feasible for use because uniform concentrations of oil could not be found at available field sites. For example, a fixed belt skimming installation originally proposed for installation at the air barrier site would not have operated efficiently due to the absence of thick oil films at that site and due to the influence of the changing river currents and wind directions on oil accumulation at that location. As the following paragraphs will show, other oil skimming devices proved not to be feasible for just the opposite reason; that is, the oil was present in too great an abundance at some sites and with too great a degree of weathering.

As previously discussed, most of the oil accumulations have been found in the upper river areas and the sampling program demonstrated that much of the surface oil can be regularly deposited along the shoreline and never reach the river mouth. To retrieve this oil, most heavily distributed along the two-mile length of the river in its most industrialized section, a portable skimmer was constructed and field evaluated. Such a skimmer on a larger scale would be preferably mounted on a self-powered, flat top barge, but our model was a self-floating unit which could be carried in a small boat and powered by a 12 volt battery.

During the 1969 and 1970 sampling periods, skimmer samples were efficiently and rapidly collected from a number of locations in the Buffalo River. However, when attempts were made to analyze these samples to provide estimates of the oil-to-water recovery ratio and to compare the nature of the rotating drum samples with those from the screen dip surface water samples (which were also being routinely obtained), it was discovered that the actual collected material from the rotating drum skimmer was quite clean water and that the skimmed oil fractions had accumulated on the rotating drum skimmer blade (almost quantitatively) as congealed, almost impossible to remove, grease.

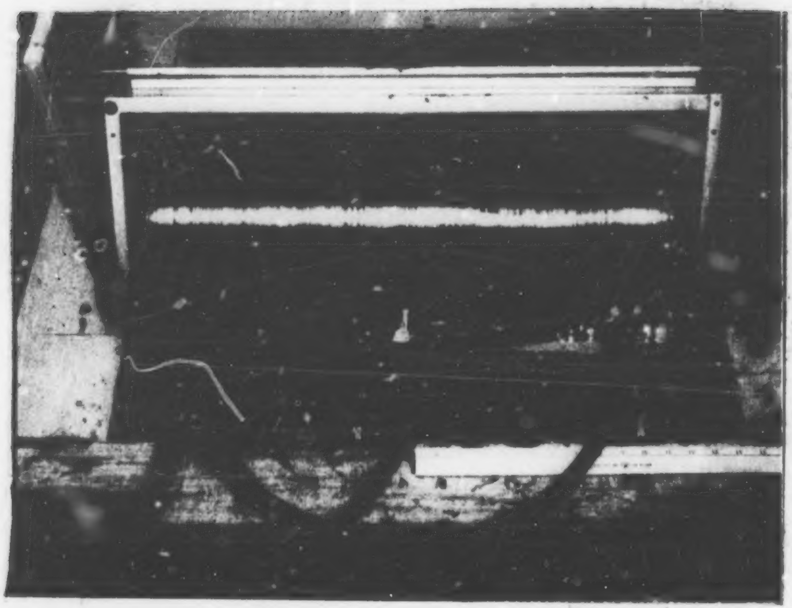
Figure 95 shows a photograph of the skimmer evaluated in the field. It consisted of a floating, free-swinging, stainless steel, chrome-plated drum, 9 inches in diameter and 24 inches long. It was turned by a nominally 12 volt DC windshield wiper motor. The gear box of the wiper motor had been modified to produce a continuously rotating shaft rather than the original reversing action of the wiper.

Figure 95 provides a photograph of this sampling skimmer after use in the extremely oil-laden waters of the industrialized section of the Buffalo River. The weathered oils and greases found in those locations congealed on the scraper blade and did not flow to the collection containers. Similarly, these thick oil slicks were noted to foul the screen device used to collect surface samples during the sampling program.

THE USE OF PISTON FILMS AS AN AID TO SKIMMER OPERATIONS

It became evident early in the program that the efficiency of any type of skimmer, be it drum type, belt type, or suction type, could be markedly improved if some technique were available for concentrating the oil and directing it to a fixed location for retrieval by the skimming or collecting device. A recent development pioneered by a group at the Naval Research Laboratory, which has widespread potential application, is the use of surface chemical displacing agents as piston films for concentrating or controlling the oil slick size and motion. These compounds are non-toxic, surface-active chemicals that compete with the oil for space at the air/water interface and in so doing, very capably guide the oil away from the point of the chemical application and thicken the slicks of oil into more readily recovered pools at locations chosen by the investigator and not by the meteorological nuances.

A demonstration of the utility of such piston films is described below, in conjunction with a test on an oil skimmer known as the Brill Skimmer. Fielded on the Buffalo River, the Brill Skimmer is basically a small, recirculating hose which drags water films (with their adhering oil layers) to a wiping device causing the oil and water mixture to drop into a collecting container. In the actual Buffalo River field tests, this skimmer design showed a very poor oil-to-water recovery ratio. For example, in the numerous field tests run in the 1969 season,



PHOTOGRAPH OF SAMPLE SKIMMER AFTER USE IN EXTREMELY OIL–POLLUTED SURFACE WATER. WEATHERED OILS AND GREASES CONGEALED ON THE BLADE AND DID NOT FLOW TO COLLECTION CONTAINERS.

Figure 95 MODEL OF ROTATING DRUM SKIMMER USED IN FIELD TESTS ON BUFFALO RIVER

the average rate of liquid collection was only about 3 quarts per hour and less than 20% by volume, of this, was oil. Nonetheless, the chronic problem remained, regardless of the initial skimmer efficiency, that the oil recovery drops to nearly zero unless the skimmer is constantly relocated to new oil-covered regions. Light oils with some oxidized components should flow readily toward any skimmer as the oil burden at the skimmer is continually depleted. But this situation is very rarely encountered on industrial waterways like the Buffalo River, or in a weathered oil spill at sea, because of the overriding effects of wind and current and the resistance of the more heavily weathered oils and emulsified surface sludges to spontaneous flow. Instead, it is more often observed that the skimmer efficiency drops to nearly zero within a few minutes after oil collection begins simply because there is no oil flowing into the immediate vicinity of the skimmer.

By the use of piston films, it was demonstrated during this program that the skimming operation at any location can be vastly improved. The piston films, spreading as monomolecular layers, compress, thicken, and drive the oily pollutants toward the operating skimmer from a large region. In one field test, for example, the following data were obtained with the Brill Skimmer mounted on a barge and used at Site No. 5, the South Park Bridge Site, the most polluted site in the Buffalo River. For the first 10-minute operating period, the skimmer operated in a pool of heavily oil-coated water, collecting 460 cc within that 10 minute period, some 70 cc of which were oil. Over the next 10 minutes, with the immediate surface area nearly depleted of oil, the skimmer collected approximately the same liquid volume but only traces of oil were present in the material collected. In the final 10 minute evaluation period, drops of a piston film forming agent were applied around the periphery of the barge. The skimmer liquid sample then measured 480 cc with 40 cc of oil collected. Thus, a potential continuation of normal or near normal skimmer efficiency can be envisioned by the use of piston films to drive oil from inaccessible locations to the location of a fixed skimmer. This concept naturally has its limits and will not by itself eliminate the need for portability of certain types of oil skimmers so that they can be relocated at will to strongly polluted areas or areas where oil spills have occurred. In particular, the piston films cannot overcome high currents or high winds. On the other hand, it is often possible to have the piston films deployed in the direction of the current and/or wind, in which case their effectiveness is even greater.

As a further demonstration of the field applicability of the piston film technique, we experimented with a reel of special floating plastic rope which contained a coating of this surface-active agent as a persistent source. The reel was mounted in a tank in such a way that as the floatable rope unwound it passed through the piston film-forming agent to achieve a uniform coating. In the field operations, the rope was unwound from the rear deck of the Harbormaster boat to encircle a large area of oil-covered surface where a sampling skimmer had been placed in the center. The rope itself acted as both the mechanical barrier and as an immediate source of the spreading agent. The rope material used was a multi-stranded, polypropylene filament which had many desirable features for this field testing. It provided a mechanical booming action because it did float at the air/water surface. It was twice as strong as manilla rope, it resisted abrasion, and was impervious to most of the industrial chemicals encountered over the field test program and did not degrade from exposure to sunlight.

It will be recalled that the piston films which had been tested on the River as aids in improving oil skimming operations were also instrumental in providing a quantitative technique for measuring the surface water quality. Thus we were able to compare empirically the effectiveness of various mechanical booms and skimmers early in this Buffalo River project. Infrared "fingerprints" taken at the identical locations before and after treatment with an oil-displacing compound demonstrated that even the grossest pollutant layers could be completely driven away from piers and shorelines. The residual surface quality of even an industrial waterway could be so improved as to match that of a typical recreational lake in the midst of the tourist season. That is not to say that either case is oil free, but that a minimally acceptable oil burden was supported in both cases.

In ancillary experiments at Cornell Aeronautical Laboratory, to assess the safety of the piston film agents to aquatic life and waterfowl, experiments were run with the culturing of brine shrimp beneath piston film-coated waters and with the provision of piston film-coated waters as the exclusive drinking and swimming source for ducks. Also, large numbers and varieties of tropical fish in common aquaria were raised in waters covered continuously by excess quantities of the surface active agents. In none of these instances has there yet been observed any adverse effect of the presence of these compounds at the water surface. Experiments with tropical fish in home aquaria have been in progress over a year, and are continuing.

CHARACTERIZATION OF TEST OILS USED IN THE SKIMMER EVALUATION FACILITY

Extensive testing of a variety of skimmer devices operating in a laboratory simulation facility was undertaken, using different interface conditions and different varieties of oil. The sampling and identification phase of the project was therefore expanded to include service characterizations for the skimmer evaluation group. The four oils selected for study and intercomparison as to their amenability to pickup by a variety of skimming devices were No. 2 Fuel Oil, No. 6 Fuel Oil, Bachaquero Crude Oil, and South Louisiana Crude Oil. These materials have the following general properties as provided to us by Mr. Leo McCarthy and Dr. Joseph Lafornara of the Hudson-Delaware Basins Office of the Environmental Protection Agency at Edison, New Jersey. No. 2 Fuel Oil had a viscosity of 2.4 centistokes, an API gravity of 32, and a universal viscosity of 135 at 100°F. The No. 6

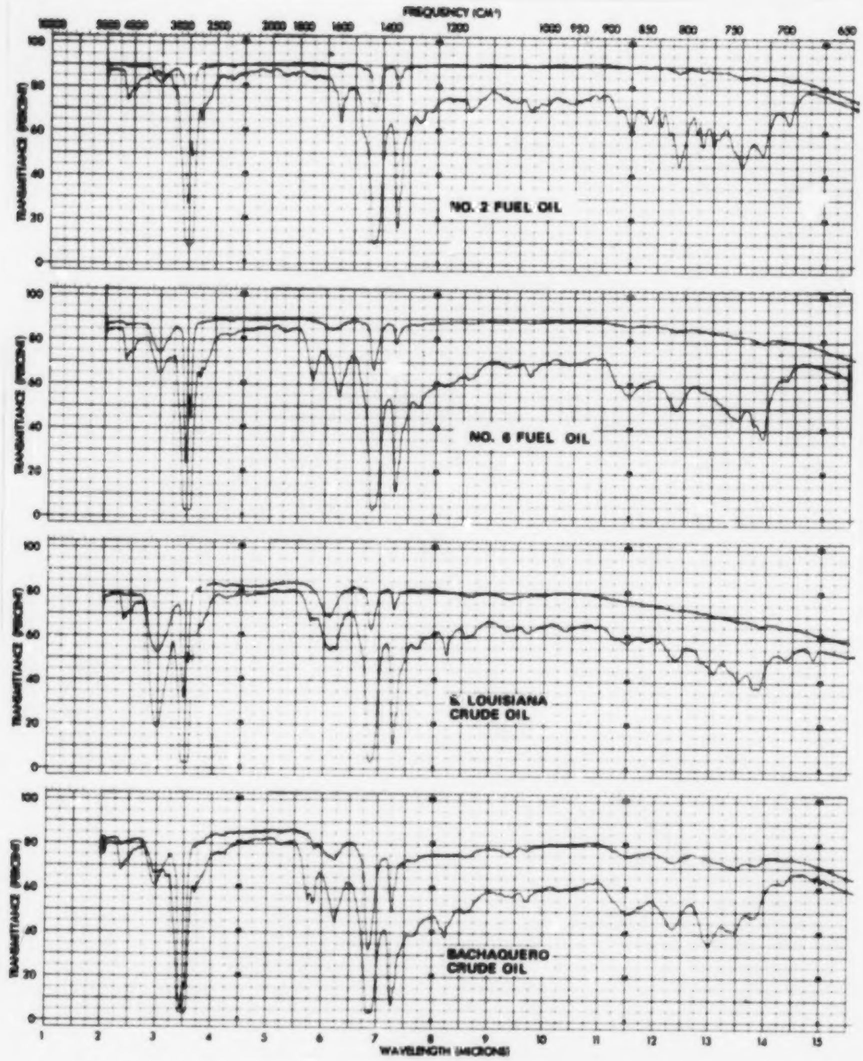
Fuel Oil had a viscosity of 887 centistokes, an API gravity of 10, and a universal viscosity of 4500 at 100°F. The South Louisiana Crude Oil had a viscosity of 4.5 centistokes, an API gravity of 36.6, and a universal viscosity of 41 at 100°F. The Bachaquero Crude Oil had an API gravity of 17, a universal viscosity of 1500 at 100°F, and its density was noted to be approximately 0.9.

Figure 96 collects conventional transmission infrared spectra of each of these oils used in the skimmer evaluation tests. The upper trace in each chart in this figure was recorded from a capillary film thickness of each sample and the lower trace in each chart was recorded for a film thickness of each sample of 0.05 mm.

Figure 97 collects infrared spectra characterizing (a) oxidized and raw No. 6 Fuel Oil used in the skimmer evaluation facility, (b) emulsified surface sludge built up during the oil skimming operations in the presence of waves and debris, and (c) bottom sediments formed at the floor of the skimmer evaluation tank quite regularly during the test operations. All spectra in this figure were recorded by the internal reflection technique. Also provided in Figure 97 is a typical spectral baseline for all traces recorded by this method. The formed gelatinous matter accumulating as sediments in the skimmer evaluation tank had an infrared absorption signature not greatly different from the baseline for the germanium prism used in the internal reflection technique. There is, however, a small band attributable to hydrocarbon at 2900 cm^{-1} and a second small band attributable to carbon-carbon double bonds at between 1640 and 1650 cm^{-1}, as shown in Figure 97.

The spectrum presented for the emulsified sludge film accumulated on the skimmer evaluation tank water surface during the oil skimming experiments shows the presence of a considerable quantity of water in the almost solid mass of this collected oil. Note, in the spectrum in Figure 97, the gross hydroxyl absorption band at 3280 cm^{-1} and relatively weak hydrocarbon bands showing through at 2980 cm^{-1}. After drying of this sludge at a higher temperature, approximately 90°C, to eliminate the infrared absorption of the labile water, the spectrum still showed evidence for an abundance of hydroxyl and carbonyl groups. An overall enhancement of the hydrocarbon group absorption at 2900 cm^{-1} resulted from the concentration effect on the oil phase by the elimination of the water.

In Figure 96, the spectra for the various test oils have the following features. With the No. 2 Fuel Oil in the two film thicknesses, capillary film and 0.05 mm, the capillary film revealed fine detail in the high absorption areas while the thicker film revealed absorptions that would go unnoticed via capillary film transmission spectroscopy or via internal reflection spectroscopy. In this particular set of traces, aside from the normal hydrocarbon absorptions, note the presence of some carbon-carbon double bond absorption at 1600 cm^{-1}. The traces given for the No. 6 Fuel Oil show, in addition to the hydrocarbon and carbon-carbon



NOTE: UPPER TRACE IN EACH CHART WAS RECORDED FROM A CAPILLARY FILM THICKNESS OF EACH SAMPLE, AND LOWER TRACE IN EACH CHART WAS RECORDED FOR A FILM THICKNESS OF EACH SAMPLE OF 0.05 mm

Figure 96 CONVENTIONAL TRANSMISSION INFRARED SPECTRA OF OILS USED IN SKIMMER EVALUATION TESTS

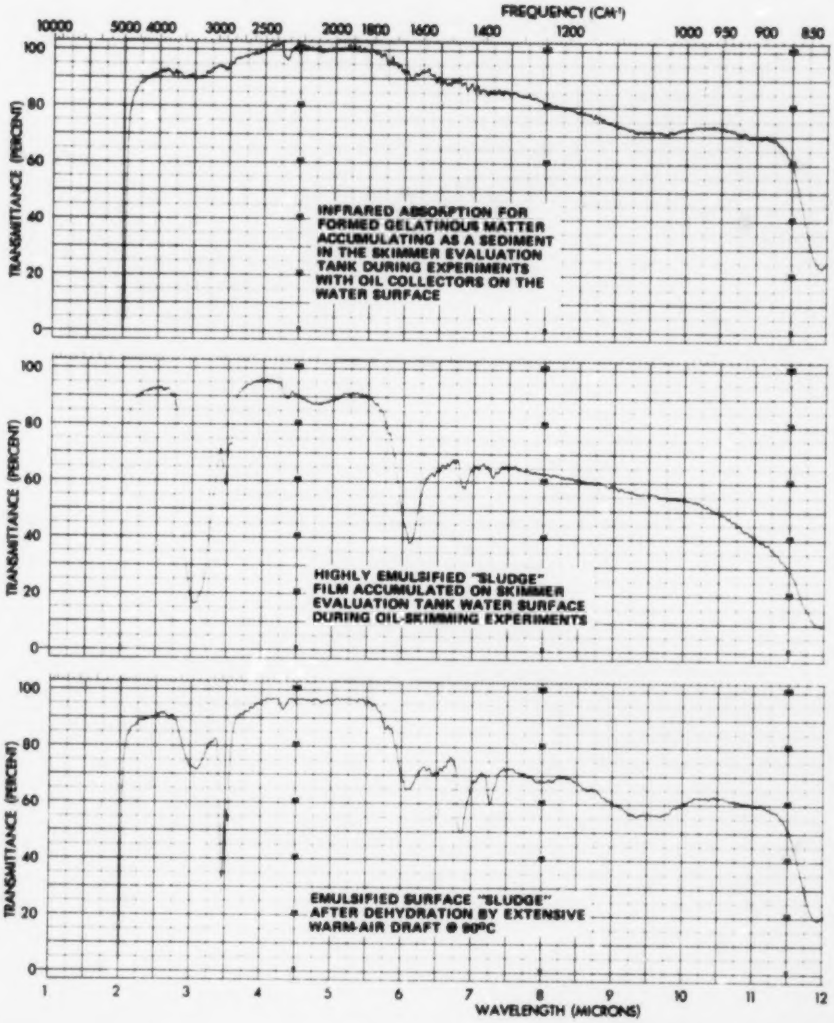


Figure 97 INFRARED SPECTRA CHARACTERIZING (1) "OXIDIZED" AND RAW FUEL OIL USED IN SKIMMER EVALUATION FACILITY, (2) EMULSIFIED SURFACE "SLUDGE" BUILT UP DURING OIL-SKIMMING OPERATIONS IN THE PRESENCE OF WAVES AND DEBRIS, AND (3) SEDIMENT FORMED AT BOTTOM OF SKIMMER EVALUATION TANK (SHEET 1 OF 2)

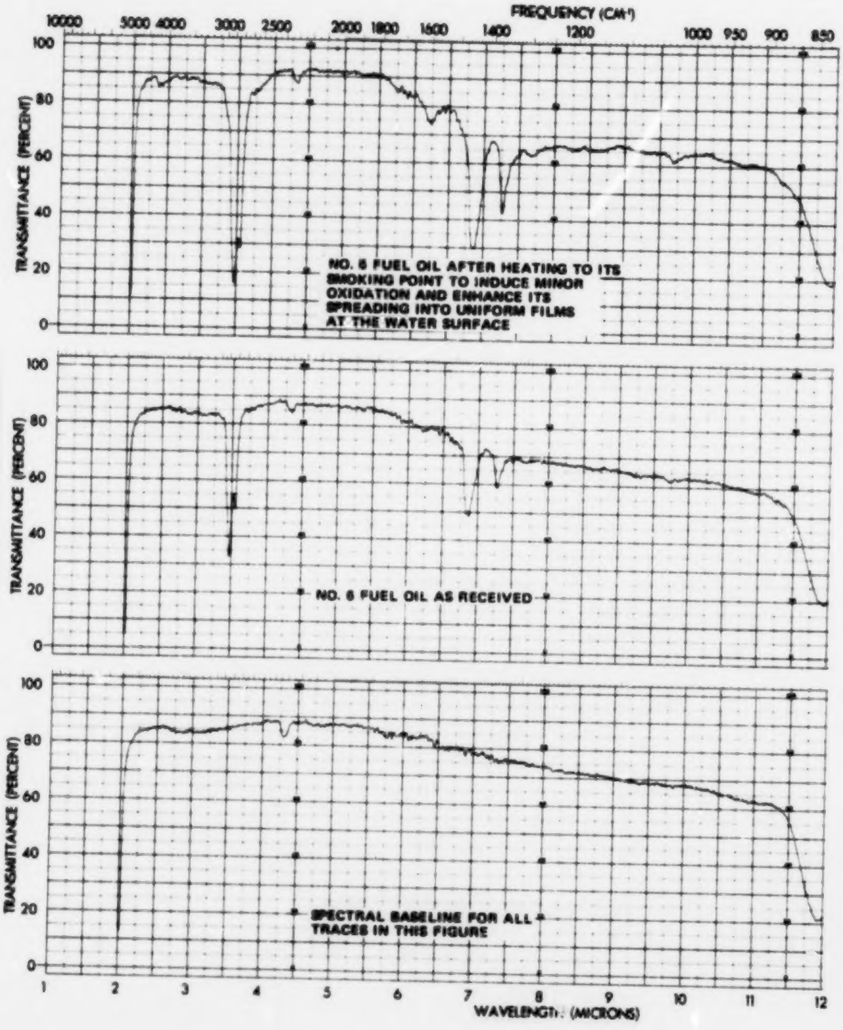


Figure 97 INFRARED SPECTRA CHARACTERIZING (1) "OXIDIZED" AND RAW FUEL OIL USED IN SKIMMER EVALUATION FACILITY, (2) EMULSIFIED SURFACE "SLUDGE" BUILT UP DURING OIL-SKIMMING OPERATIONS IN THE PRESENCE OF WAVES AND DEBRIS, AND (3) SEDIMENT FORMED AT BOTTOM OF SKIMMER EVALUATION TANK (SHEET 2 OF 2)

double bonds, an additional quantity of carbonyl material, (carbon double bonded to oxygen) in absorptions of 1735 cm^{-1} and for hydroxyl groups (that is oxygen bonded to hydrogen) at between 3340 and 3350 cm^{-1}. The South Louisiana Crude Oil had a spectrum similar to that for the Bachaquero Crude except for an additional very large hydroxyl absorption at 3350 cm^{-1}. In the Bachaquero Crude itself all of the spectral peaks noted in the No. 6 Fuel Oil were present and in addition the carbonyl band was doubled, that is, its frequency was split at 1711 cm^{-1} and 1739 cm^{-1} indicating the presence of at least two different types of carbonyl groups.

In these four sets of spectra, differences in the traces in the regions between 1225 and 950 cm^{-1} are related generally to the degree and type of aromatic substitution in the aromatic components present in each of these fuel mixtures.

These analyses were necessary to the performance of the Buffalo River project, since they provide the chemical identifications of the products which were subjected to skimming tests. Petroleum compounds which do not fit into the classes described above cannot be assumed to behave similarly in skimming operations.

CASE STUDIES OF THE APPLICATION OF THE DEVELOPED IDENTIFICATION METHODS TO CITY, STATE, AND FEDERAL NEEDS FOR OIL POLLUTANT ANALYSIS

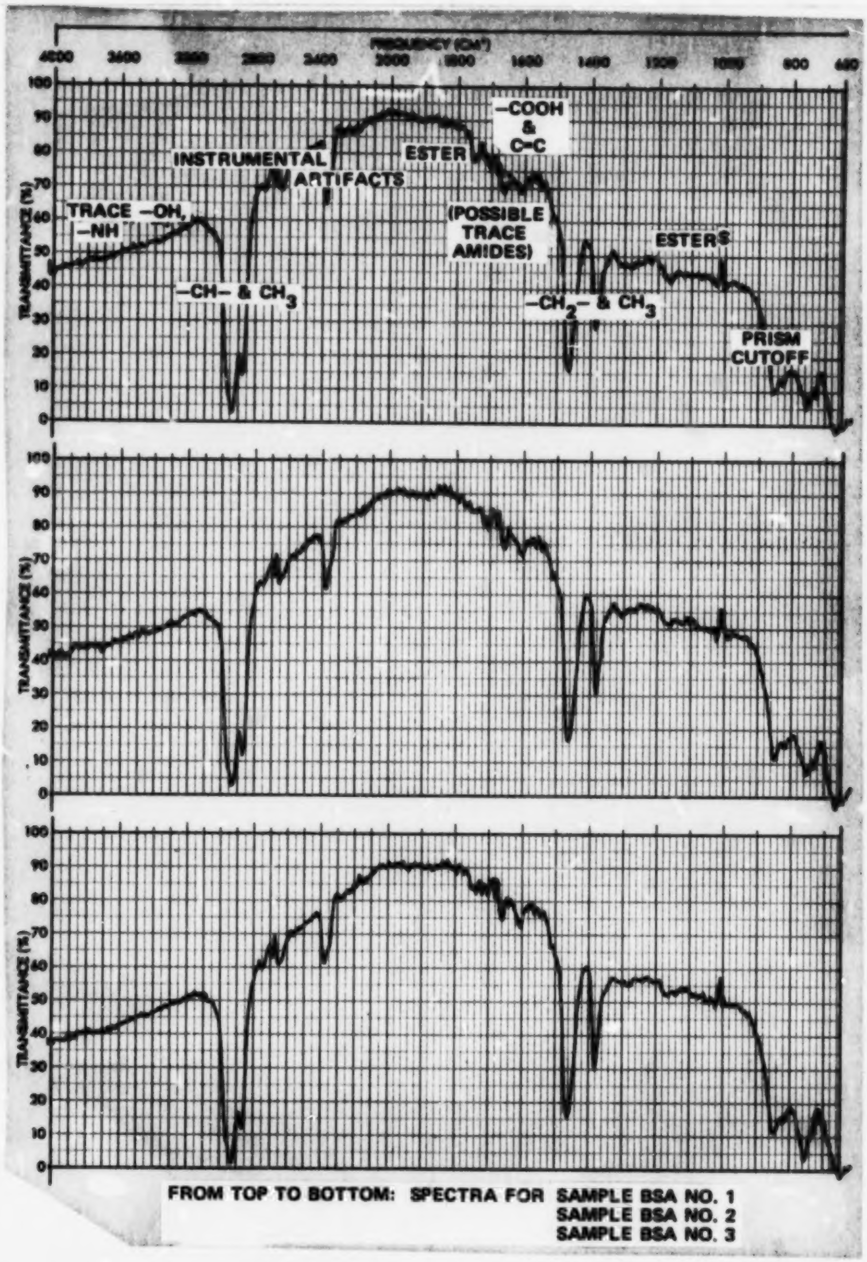
Over the course of the Buffalo River project, a feature of special value to the local Western New York community and to State and Federal agencies became apparent in the new and focused capability of the Cornell Aeronautical Laboratory to provide rapid response to the occasional needs for analysis of oily pollutants. A good working relationship was established among the following parties in addition to Cornell Aeronautical Laboratory itself: (1) the City of Buffalo Engineer's Office, (2) the Buffalo Sewer Authority Analytical Laboratory, (3) the New York State Department of Environmental Conservation, (4) the New York State Department of Health, (5) Harbormaster of the City of Buffalo, (6) the Great Lakes Laboratory of the State University College at Buffalo, (7) the U.S. Geological Survey, (8) the Water Quality Group at the Federal Water Quality Office in Edison, New Jersey, (9) the Regional Office of the Environmental Protection Agency, and (10) the Interface Chemistry Section at the Naval Research Laboratory in Washington, D.C. During some or all parts of the sampling and analysis phase of the Buffalo River project we have shared knowledge and technical facilities with these groups and occasionally have shared man power as well. With the Buffalo Sewer Authority Chemical group, in particular, we have routinely split the analytical load for the large number of samples retrieved for the Buffalo River survey and have developed a mutual trust and confidence in one another's analytical results through analysis of replicate samples provided as unknowns between these laboratories.

The following paragraphs describe the application of the methods and techniques developed for the Buffalo River oil survey program to the "trouble shooting" needs of various of these agencies over the last two year period. The Buffalo River project did not bear the expense for those analyses, however, since they were provided as a public service by Cornell Aeronautical Laboratory for the agencies involved.

CASE NO. 1: ANALYSES OF "UNKNOWN" SAMPLES ASSOCIATED WITH AN OIL SPILL INCIDENT ON THE BUFFALO RIVER

The following figures and tables provide documentation on oil sample analysis associated with a spill of fuel oil into the Buffalo River from a railroad refueling operation. The samples received by the Cornell Aeronautical group were unknowns labelled only as BSA No. 1, BSA No. 2 and BSA No. 3.

Responding to the urgent need for a rapid identification of these materials, the preliminary analyses by the infrared internal reflection spectroscopic technique were completed on the evening that the samples arrived. Copies of the rapidly and inexpensively produced infrared spectra using the internal reflection technique are given in Figure 98. The preliminary indications from these spectra were that sample BSA



FROM TOP TO BOTTOM: SPECTRA FOR SAMPLE BSA NO. 1
SAMPLE BSA NO. 2
SAMPLE BSA NO. 3

Figure 98 RAPIDLY AND INEXPENSIVELY PRODUCED INFRARED SPECTRA, USING THE INTERNAL REFLECTION TECHNIQUE, FOR PRELIMINARY ANALYSES OF "UNKNOWN" SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON THE BUFFALO RIVER

No. 1 was different from the other two samples in that it contained some fraction of oil of probable biological origin. The other two samples were seemingly both oils of petroleum origin, but these preliminary spectra could not differentiate between them as to their sources or histories other than that neither had been intimately mixed with biological fluids. The more careful subsequent work confirmed the results from these initial rapid scans in that sample BSA No. 1 was shown to be different from the other two specimens by incorporating a small fraction of esterified hydrocarbons in addition to its dominant portion of unoxidized hydrocarbons which were common to all three samples. The range assessable by the rapid infrared technique was limited to wavelengths less than 10 microns by the cut-off frequency of the prisms used. The samples BSA No. 2 and BSA No. 3 could not be discriminated from one another within this range. These early spectra did not eliminate the possibility that the major portion of BSA No. 1 was identical to either or both of No. 2 or No. 3, but these early spectra did show that sample No. 1 had a different history most likely including admixing with esterified hydrocarbons of biological origin as were found commonly in other oil samples retrieved during this program from the sanitary sewers and their overflows. It was later learned from the Buffalo Sewer Authority chemists that sample BSA No. 1 had indeed been collected from a sewer overflow which was suspected to be the origin of the oil spill.

More complete infrared analyses using the standard transmission methods, which required more time-consuming procedures, were employed in recording the infrared spectra gathered in Figure 99. Each of the samples was prepared both as a capillary film and as a 0.05 mm thick film between salt crystals and scanned using the conventional infrared transmission spectrophotometric methods. The scan range extended from 2.5 microns through 15 microns, notably including the aromatic fingerprint region from 12 to 14 microns.

Table 20 provides a complete listing of the significant absorption bands noted for each specimen and the apparent correlation for each band with specific chemical groupings. It will be noted from a review of the listing in Table 20, and of the infrared spectra themselves in Figure 99, that in the region between 5 and 6 microns the difference of sample BSA No. 1 from BSA No. 2 and No. 3 is quite clear. BSA No. 1 contains a strong ester band at 5.75 microns which is absent or very weak in the other two specimens. However, as one compares the presence and intensities of bands around 11.85, 12.24, 12.75, 13.0 and 13.5 microns it becomes clear that BSA No. 1 and BSA No. 3 are strikingly similar to one another in their aromatic components. Such similarity in aromatic constituents is usually specific to hydrocarbons from the same source. It is also clear that samples BSA No. 1 and BSA No. 3 were different in this regard from BSA No. 2. In the tabulation of Table 20, where the remarks "strong" and "weak" are recorded, these remarks are meant only to compare the relative band intensities within the spectra herein compared and are not to be taken in an absolute sense.

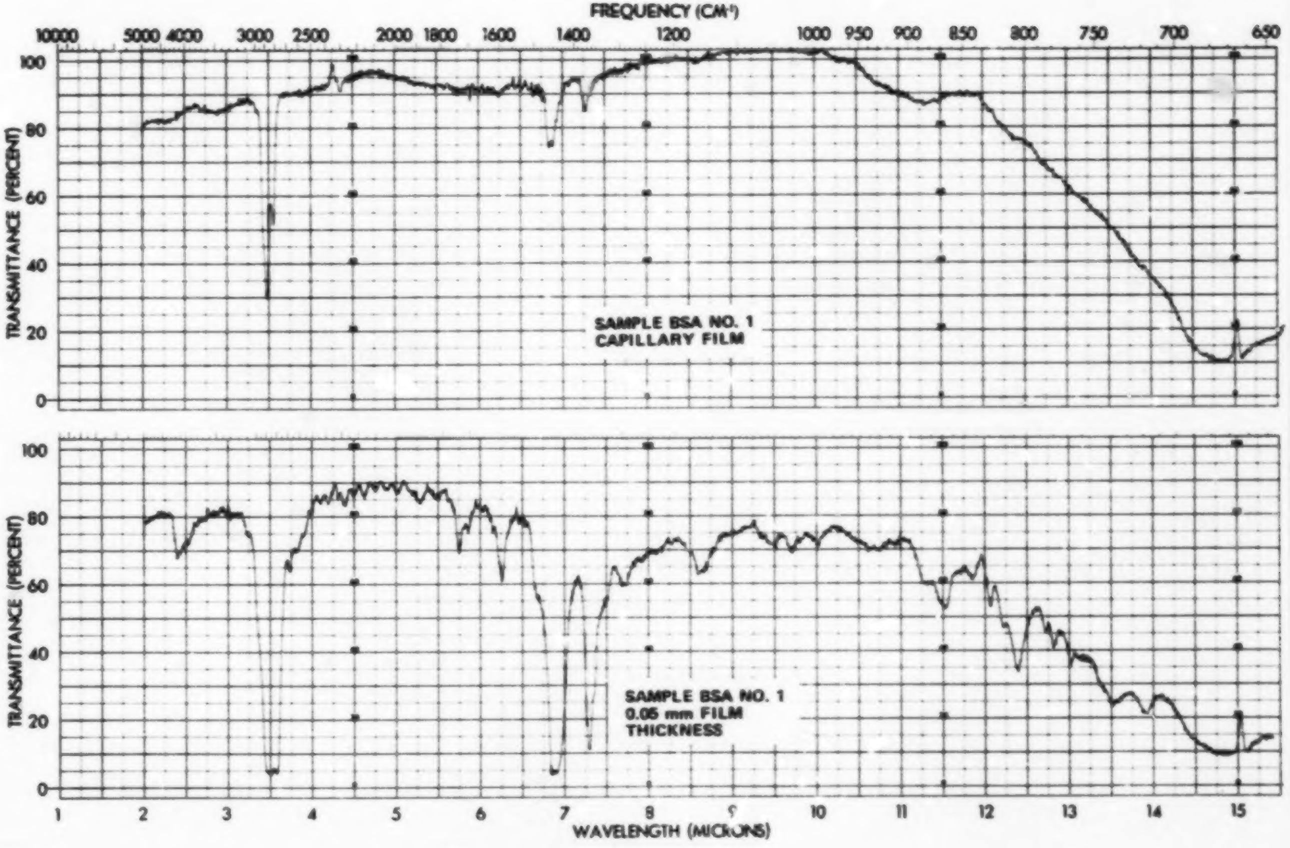


Figure 99 TRANSMISSION INFRARED SPECTRA OF "UNKNOWN" SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON THE BUFFALO RIVER (SHEET 1 OF 3)

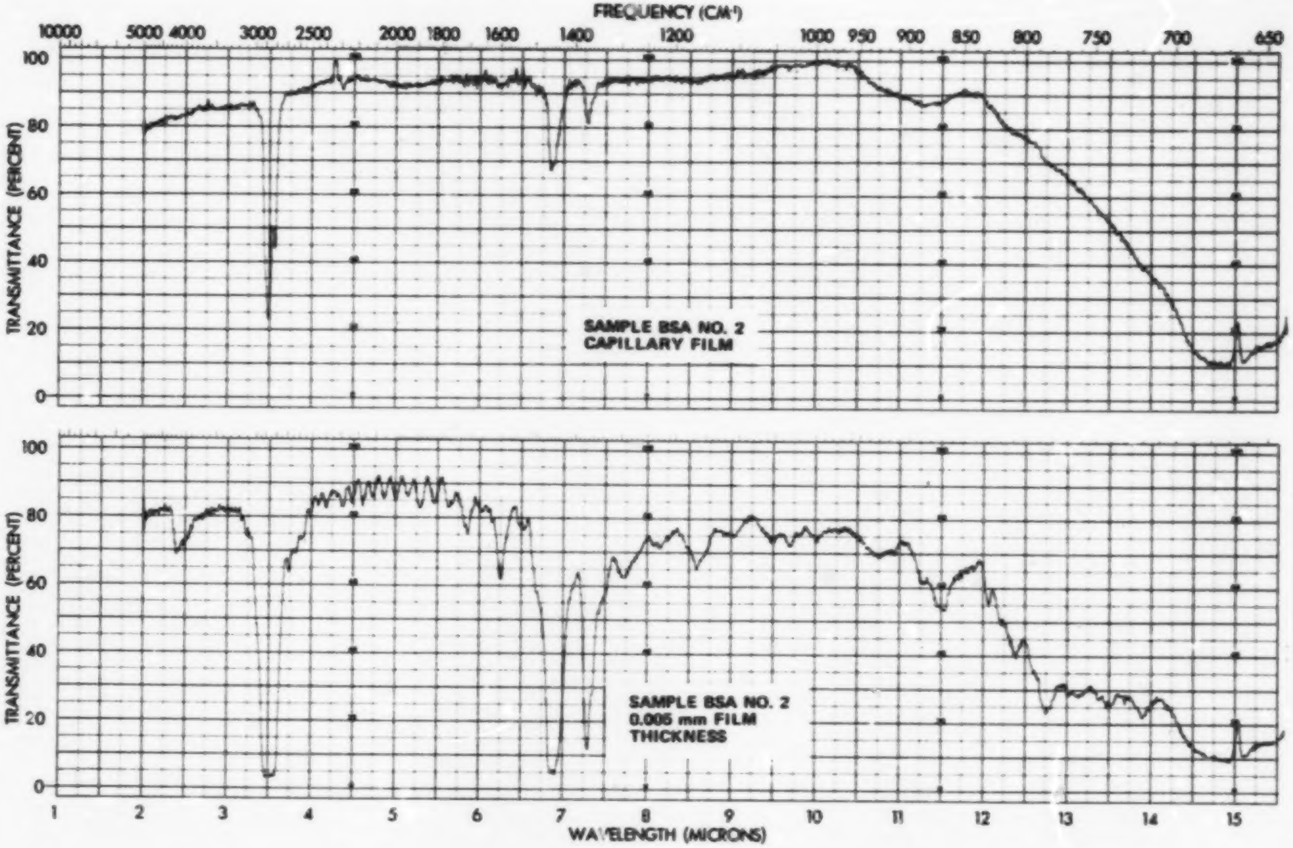


Figure 99 TRANSMISSION INFRARED SPECTRA OF "UNKNOWN" SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON THE BUFFALO RIVER (SHEET 2 OF 3)

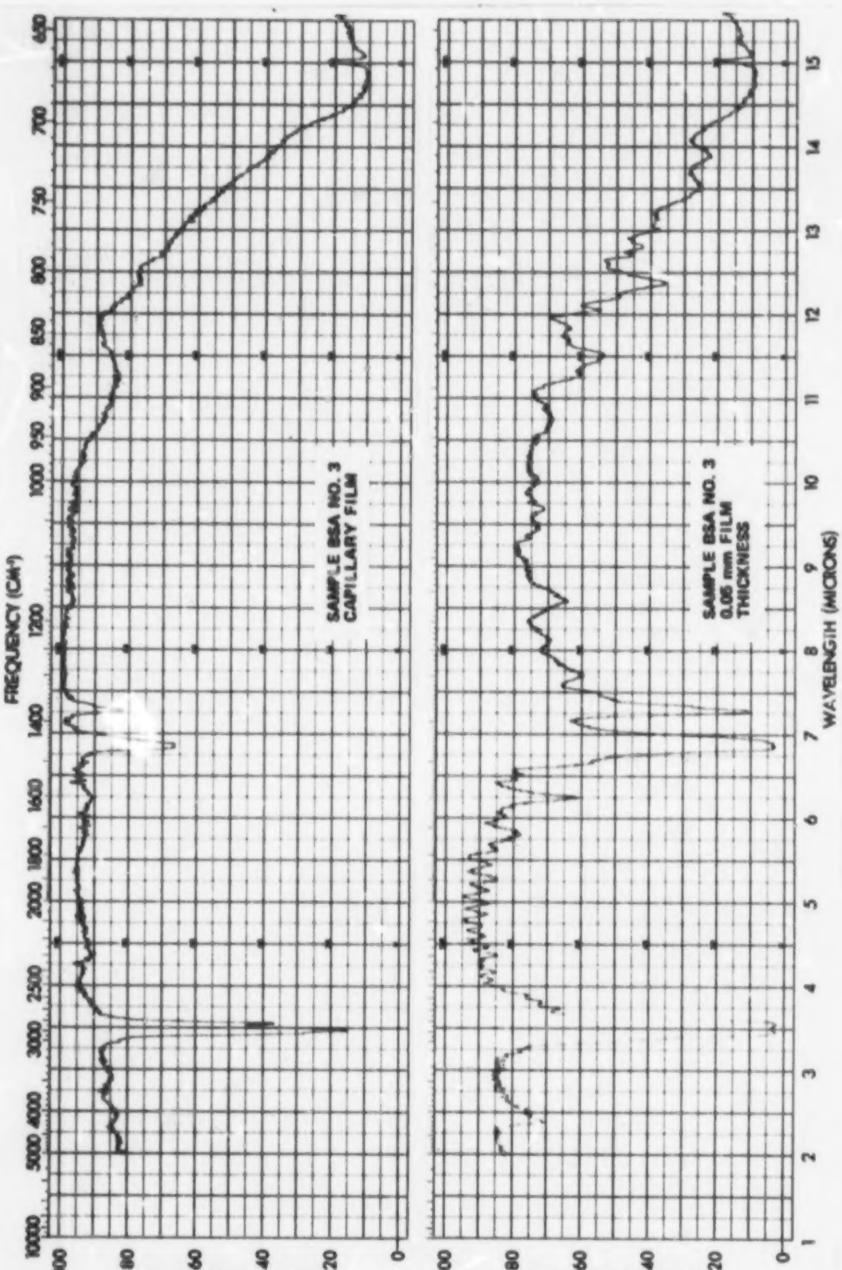
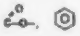
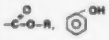
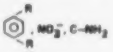
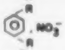
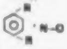


Figure 99 TRANSMISSION INFRARED SPECTRA OF "UNKNOWN" SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON THE BUFFALO RIVER (SHEET 3 OF 3)

Table 20
SIGNIFICANT ABSORPTION BANDS NOTED IN INFRARED SPECTRA OF SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON BUFFALO RIVER

APPROXIMATE WAVELENGTHS (MICRONS)	CHEMICAL GROUPS INDICATED	BSA NO. 1	BSA NO. 2	BSA NO. 3
3.5	$-CH_2-$, $-CH_3$	X	X	X
5.6		X	X	X
5.75	$-\overset{O}{C}-O-R$	STRONG X	–	WEAK X
5.85	$-\overset{O}{C}-H$, $\overset{O}{C}-OH$	WEAK X	STRONG X	STRONG X
6.25		X	X	X
6.6		X	X	X
6.85	$-CH_2-$	X	X	X
7.2	$-\overset{\vert}{\underset{\vert}{C}}-CH_3$	X	X	X
7.5	$>NH$	X	X	X
7.7	$-CH_3-Si-$	X	X	X
8.1		–	X	X
8.6		X	X	X
9.1	$>NH$	–	X	WEAK X
9.5	$-C-O-H$	X	X	X
9.7	$-C-O-$	X	X	X
10.0	$-CH=CH_2-$	X	X	X
10.7	$-\overset{O}{C}-OH$	X	X	X
11.3	$-NO_2$, $CO_3^=$, $-C=C\langle^{R}_{R}$	X	X	X
11.5	$-NO_2$, $CO_3^=$, $-C=C\langle^{R}_{R}$	X	X	X
11.85	$-C-NH_2$, $CO_3^=$	X	–	X
12.1	NO_3^-, $C-NH_2$	X	X	X
12.2		X	X	X
12.4		STRONG X	WEAK X	STRONG X
12.75		WEAK X	STRONG X	WEAK X
13.0		STRONG X	WEAK X	STRONG X
13.5		STRONG X	WEAK X	STRONG X
13.9	$-CH_2-$	X	X	X
14.7		X	X	X

The conclusion from the infrared studies was the following: BSA No. 1 and BSA No. 3 represent oil from a similar (not necessarily identical) source, but BSA No. 1 has in addition become admixed with a small quantity of oxidized hydrocarbon of biological origin. BSA No. 2 is a sample containing oil of a type similar to that of BSA No. 3 but likely from a different source. After these analyses were completed it was learned from Buffalo Sewer Authority chemists that samples BSA No. 2 and BSA No. 3 were fuel oils collected from different fueling stations in two separate sections of the City as likely candidates for the formation of the oil slick observed.

Gas chromatography of each of the samples and of a variety of standards showed the following, as documented in the copies of the original chromatograms given in Figure 100. Samples BSA No. 1 and BSA No. 3 contained similar small quantities of the same low boiling components and also showed essential peak for peak identity over the whole remainder of the temperature range program which extended to 300°C. Except for some small differences in the low boiling components which could easily be ascribed to moderately different thermal histories, BSA No. 1 and BSA No. 3 were also markedly similar to a No. 2 Fuel Oil standard as we have found commonly used by the local Western New York railroads in their refueling operations. In contrast, gas chromatography of sample BSA No. 2 showed a very high content of very low boiling components, an absence of moderately low boiling components, and a higher boiling point fraction which was otherwise similar to both samples BSA No. 1 and BSA No. 3 and to No. 2 Fuel Oil as well. This observation suggests that BSA No. 2 was a similar material from a different source or location than that of BSA No. 1 and No. 3. The suggestion was further affirmed by the observation that sample BSA No. 2 had a significantly higher concentration of associated elemental iron than did the other two samples as documented in Table 21, which reports the results from the application of atomic absorption spectrometry to these "unknown" samples. Atomic absorption spectrophotometry was performed on samples BSA No. 1, BSA No. 2 and BSA No. 3 at a series of different dilutions in methyl isobutyl ketone. Six elements were selected for this initial check and intercomparison. The results of these analyses are reported in tabular form in Table 21. Samples No. B and No. L are included for comparison and represent specimens from an alleged oil spill on the Niagara River occurring within a week of the Buffalo River oil spill noted here and which are discussed in greater detail in the next case study. Note particularly in Table 21 how distinct samples BSA No. 1, 2, and 3 are as a set from No. B and No. L as a set. The wear metal content of the BSA samples is too low to indicate that any of these materials, with the possible exception of BSA No. 2, had ever been used in either a lubricating or machine operation.

Surface tensions of the various samples were estimated by use of a simple laboratory test which we have developed called the "Teflon Test." This test takes only a few, tiny droplets of material and is accurate within about 5%. The estimated liquid/vapor surface tension of all three of the BSA specimens was 24 dynes/cm, a typical value for a light

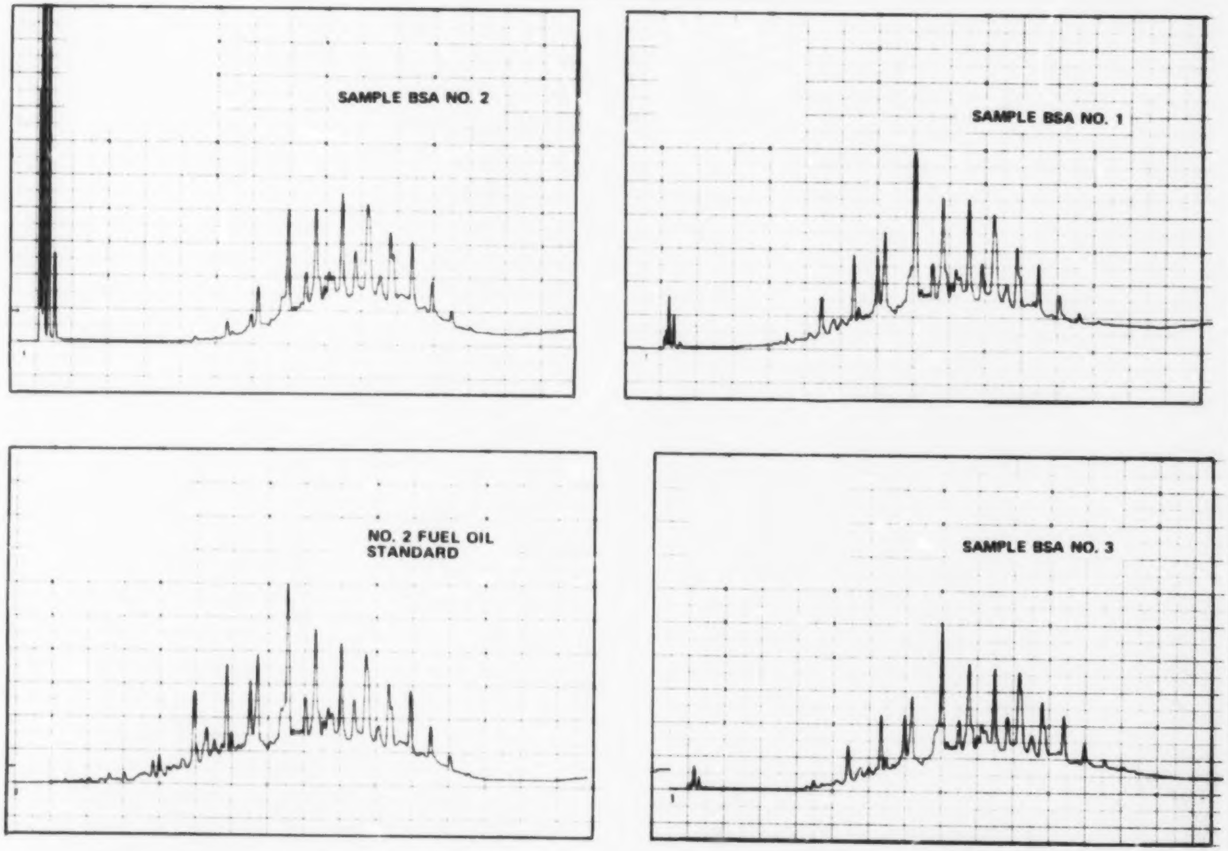


Figure 100 GAS CHROMATOGRAMS OF NO. 2 FUEL OIL STANDARD, AND OF THREE "UNKNOWN" SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON THE BUFFALO RIVER

Table 21

RESULTS FROM APPLICATION OF ATOMIC ABSORPTION SPECTROSCOPY TO ANALYSIS OF "UNKNOWN" SAMPLES ASSOCIATED WITH OIL SPILL INCIDENTS ON THE BUFFALO AND NIAGARA RIVERS

SAMPLE	ELEMENT CONCENTRATIONS IN OIL SAMPLES (PPM)					
	IRON	CHROMIUM	MAGNESIUM	COPPER	NICKEL	SILVER
BSA NO. 1	67	2.5	0.95	0.85	0.5	nil
BSA NO. 2	134	2.8	1.5	1.10	0.45	nil
BSA NO. 3	81	3.7	1.8	0.90	0.65	nil
NO. B	680	17.0	10.0	2.5	3.0	nil
NO. L	560	17.0	8.8	3.6	1.8	nil

fuel oil. In contrast, sample No. L had a surface tension estimated to be 26 dynes/cm and sample B had a surface tension estimated to be 25 dynes/cm. These higher values indicate a different distribution of hydrocarbon chain lengths favoring the longer chains most often found in cutting oils. At the other extreme, a very light lubricating oil, such as "3 in 1 oil" gives an estimated surface tension of only 23 dynes/cm which reflects the deliberate addition of very-short-chain hydrocarbons to these products to give them an immediate, rapid spreading over the surfaces to which they are applied. An equally valid parameter which could characterize the surface properties of these oils would be their "equilibrium spreading pressures," which would indicate the tendency of the oil to distribute itself over the water surface into a very thin, easily assimilated oil slick.

In summary, the samples delivered to us as having been alleged to have been associated with the oil spill incident on the Buffalo River were analyzed sequentially by internal reflection infrared spectroscopy, by standard transmission infrared methods in capillary and 0.05 mm thick films, by gas chromatography, by atomic absorption spectroscopy, and by surface chemical methods. The equipment used for such characterization is listed below:

1) Hewlett-Packard Model 5750B Dual Flame Ionization Detector Gas Chromatograph.
2) Perkin-Elmer Model 21 Infrared Spectrophotometer
3) Perkin-Elmer Model 700 Infrared Spectrophotometer
4) Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer
5) Rame-Hart NRL Model Contact Angle Goniometer.

Within the limits described in preceding paragraphs, samples BSA No. 1 and BSA No. 3 were indicated to be most similar and likely derived from the same original source. Sample BSA No. 2 was shown to be a material of basically similar chemical type, but most probably from a separate source. No two samples showed exact identity by all criteria applied. Some ambiguity persists in attempts to interrelate these samples. However, the considered opinion of a professional analyst reviewing these data would be that all three samples represented a product which could best be described as a No. 2 Fuel Oil and that sample BSA No. 1 was different from the other two in its history of having been associated with the sewage stream at some time in its recent past. Samples BSA No. 1 and No. 3 are similar enough by gas chromatographic and infrared criteria (especially by their associated aromatic components) and by their trace metal patterns, to support an action identifying them as from the same original source. The Environmental Conservation Department of the State of New York has informed us that an enforcement action has been taken and agreed to by a local railroad. The evidence accumulated is sufficiently valid to be used in court, but a court test of its applicability has not yet been made.

CASE NO. 2: ANALYSES OF SAMPLES ASSOCIATED WITH AN OIL SPILL INCIDENT ON THE NIAGARA RIVER

In late December of 1970, two samples delivered to Cornell Aeronautical Laboratory were reported to have been associated with an oil spill into the Niagara River from the outfall servicing a major automobile manufacturer. The samples were "unknowns" and described only as follows: Sample L and Sample B. Sample L was predominantly clear water on top of which was an oily layer of about 2 mm thickness. Sample B contained predominantly clear water which supported a black, oily layer of about 2 cm thickness. In both samples there was also a substantial amount of sediment and some neutrally buoyant, small oily "globs." The latter observation suggests the presence of some emulsifying agent. The suggestion that some deliberate emulsifier/dispersant might have been added, provided sufficient reason for some surface chemical tests on this material in addition to tests by infrared and gas chromatographic techniques. At the completion of these analyses, almost all of the original samples remained and they were subsequently retrieved by a representative of the Environmental Conservation Department of New York State and made available to the automobile firm, which had been cited, for their independent analyses.

Figure 101 presents the rapidly and inexpensively produced preliminary infrared spectra which showed the basic identity of the two oil samples associated with the oil spill incident on the Niagara River. More definitive gas chromatographic and infrared analyses were done as follows: Oil and a trace of water which could not readily be removed, from Sample B, was diluted 1 to 1 with carbon tetrachloride and then gas chromatography was performed on the samples. After desolvation, IR spectra of the resultant oils were run using capillary and 0.05 mm thick films between salt (NaCL) plates.

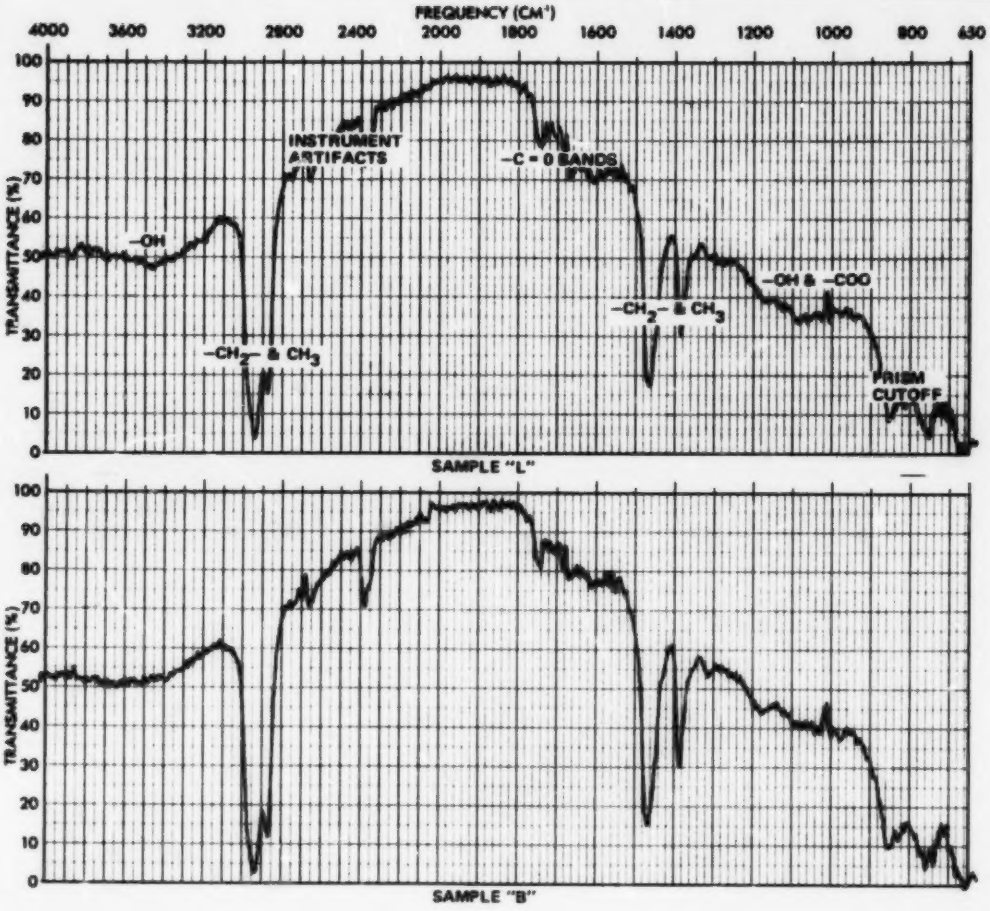


Figure 101 RAPIDLY AND INEXPENSIVELY PRODUCED PRELIMINARY INFRARED SPECTRA SHOWING IDENTITY OF TWO OIL SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON NIAGARA RIVER

Oil from Sample L could not be directly obtained free of rather large amounts of water because of the thinness of the oily layer present. Thus, an aliquot of sample L was centrifuged for 5 minutes at 1200 rpm followed by extraction of the sample surface layer with chloroform, driving off the chloroform by gentle warming, and then dilution of the oil so concentrated 1 to 1 with carbon tetrachloride. This mixture was injected into the gas chromatograph and, after desolvation, was used to prepare capillary and 0.05 mm thick films for transmission infrared analysis. All extraction apparatus used in handling and preparing these samples was precleaned with chloroform and all gas chromatograph sampling syringes and all infrared prisms were precleaned with carbon tetrachloride. The preliminary infrared spectra recorded by the internal reflection infrared technique and presented in Figure 101 have the additional advantage that they were obtained on the samples "as-received" and so are free from potential artifacts which may have been introduced into the sample preparations for the more detailed, subsequent investigations. Gas chromatography showed an essential identity between samples L and B with the single exception that there was a presence of trace amounts of low-boiling components in sample B which were not present in sample L. These components could have easily been lost from sample L during the gentle warming step required to drive off the chloroform used in the extraction process which was not required for sample B.

In addition to noting the similarity of samples L and B, it is also important to mention that they were markedly different from our standard samples of diesel fuel, No. 2, No. 4, No. 6 Fuel Oils and from Crude Oils of Louisiana and Venezuelan origin. They are also different, as will be evident by an intercomparison of Figures 102 and 100, from oil samples alleged to have been associated with an oil spill on the Buffalo River within a week of the oil spill under consideration here. The transmission infrared analyses also showed essential identity between samples B and L, with the single exception that sample B contained a trace amount of water which was carried along with the oily layer as it was sampled. The chloroform extraction of sample L eliminated traces of water from that sample. In the 0.05 mm thick films of both samples, the absorptions which appear in the 5 - 6 micron region represent oxidized hydrocarbon groups (mainly carbonyls) and the bands between 6 and 6.5 microns represent carbon-carbon unsaturation (that is, carbon double-bonded to carbon). These bands most likely correlate with oxidation of the oil during industrial use but could harbor, as well, contributions from compounds of the emulsifier/dispersant type. Results from atomic absorption spectrometry studies, which probed for specific metallic elements intimately associated with the oils, are most important for determining the origin and history of the oily samples. These results are included in Table XXI where values from the three samples alleged to be associated with the spill on the Buffalo River are also included for comparison. Although samples B and L are not perfectly identical, both have extremely high concentrations of typical

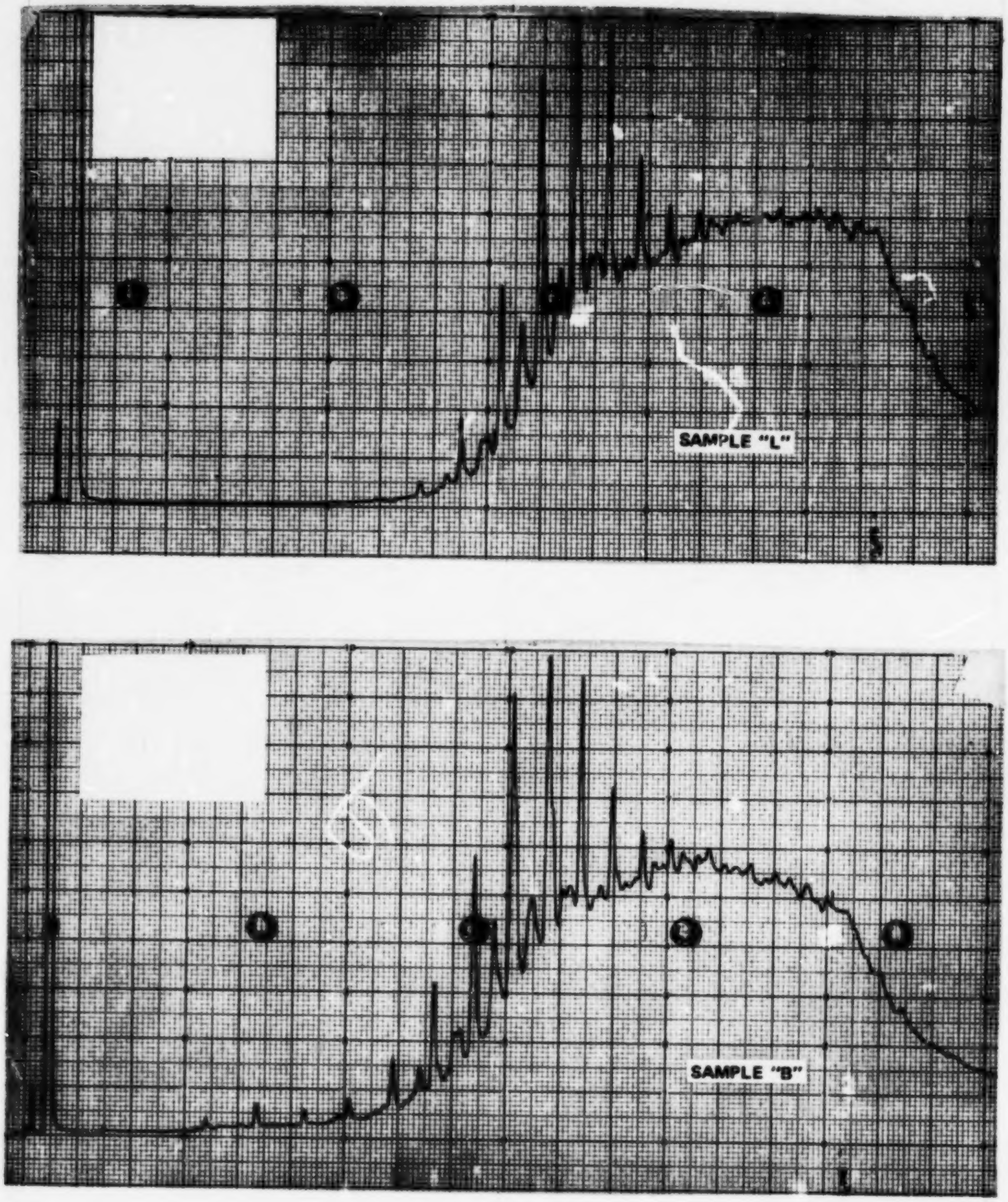


Figure 102 GAS CHROMATOGRAMS SHOWING IDENTITY OF TWO SAMPLES ASSOCIATED WITH OIL SPILL ON NIAGARA RIVER

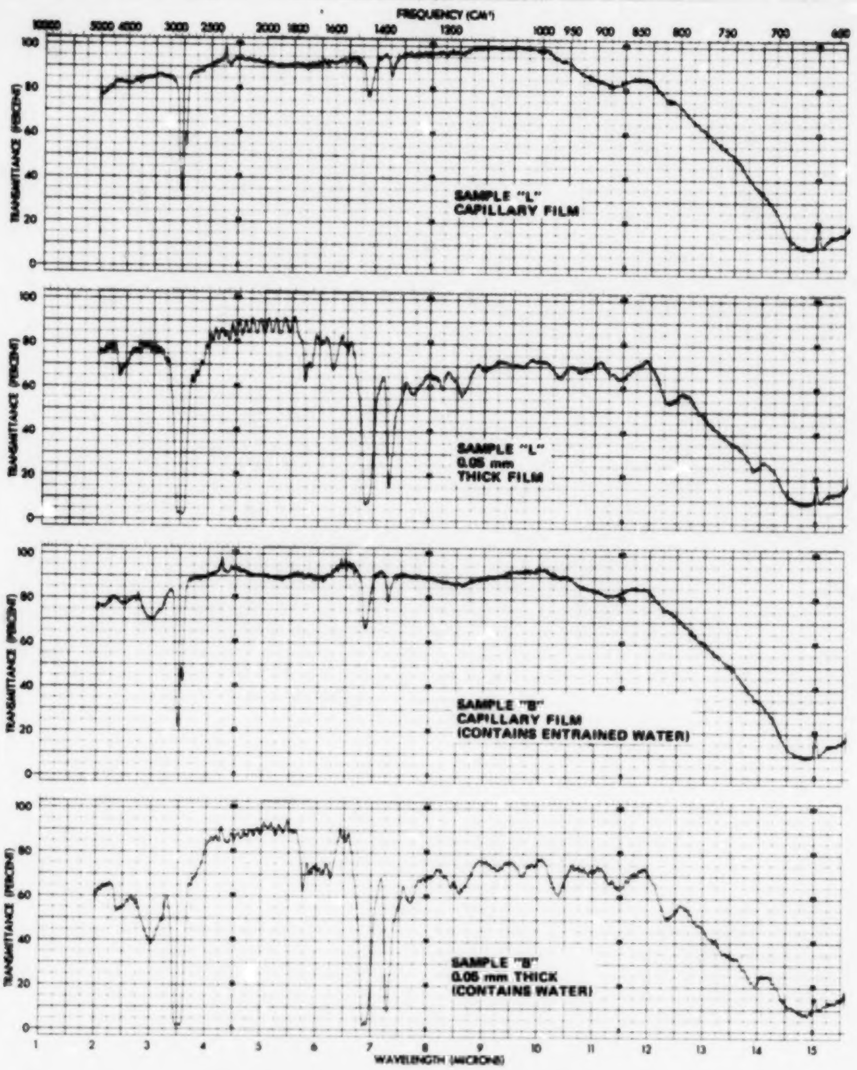


Figure 103 TRANSMISSION INFRARED SPECTRA OF CAPILLARY AND 0.05 mm THICK FILMS OF OIL SAMPLES ASSOCIATED WITH OIL SPILL INCIDENT ON NIAGARA RIVER

wear metals. Their strong difference from the other samples suggest a common origin for samples B and L at a source where substantial metallic contact was achieved. Lubricating or machining of ferrous metals is one suggested prior use for these materials.

CASE NO. 3: EXAMINATION OF SAMPLES OF TROUBLESOME COLORED INFLUENTS TO THE BUFFALO SEWAGE TREATMENT PLANT AND OF COLORED INDUSTRIAL EFFLUENTS BEING DISCHARGED OVER THE SAME TIME PERIOD

In June and July 1970 there were sporadic instances of brightly colored influents to the sewage treatment plant, which were interfering with both analyses of the inflow contents and with the effective functioning of the sewage treatment processes. Three samples delivered to the Cornell Aeronautical Laboratory by our counterparts at the Buffalo Sewer Authority had colors of pink, dark green and a lighter green. The left-hand side of Figure 104 gives infrared spectra which characterize each of these sewage influents. The prominent central bands at 1650 and 1550 cm^{-1} are associated with the proteinaceous components of this sewage. Other bands might be partially attributable to sewage components and partially attributable to colored components which were giving difficulty with these particular influents. Since the Buffalo River sampling program was at its most intense period during the same dates, it was a rather direct matter to take from our collection of samples of industrial effluents (being discharged into the Buffalo River) examples of materials with the same colors observed in the sewage input. Their spectra are recorded for comparison as potential sources of the troublesome colored material. The infrared spectra shown in the right-hand column of Figure 104 are characteristic of a pink effluent from a chemical plant, a green effluent from a steel plant and a yellow-brown effluent from a chemical plant which were being discharged on a rather regular basis over the June-July, 1970 period. The particular examination of these materials was not carried further since the problem was self-correcting as time proceeded and the sewage returned to its natural colorless state. However, the combination of spectra illustrated in Figure 104 show very clearly that, if the problem had continued, tracing of the colored components in the sewage influents could be followed all the way to certain of the chemical-based industries which occasionally feed materials into the sanitary sewer lines.

CASE NO. 4: PRELIMINARY ANALYTICAL RESULTS ON OIL SAMPLES ASSOCIATED WITH A MASSIVE OIL SPILL ON THE SCHUYLKILL RIVER

The Edison Laboratory of the Federal Water Quality Office requested a rapid infrared analysis of samples in the following case.

In November, 1970 a very large oil spill occurred into the Schuylkill River in Pennsylvania from the breaking of rain-weakened lagoons containing large quantities of waste oils. Figure 105 records preliminary infrared spectra showing the essential identity of seven specimens from waste oil storage lagoons and from the river surface as collected by EPA personnel during this oil spill incident. In Figure 105, the first

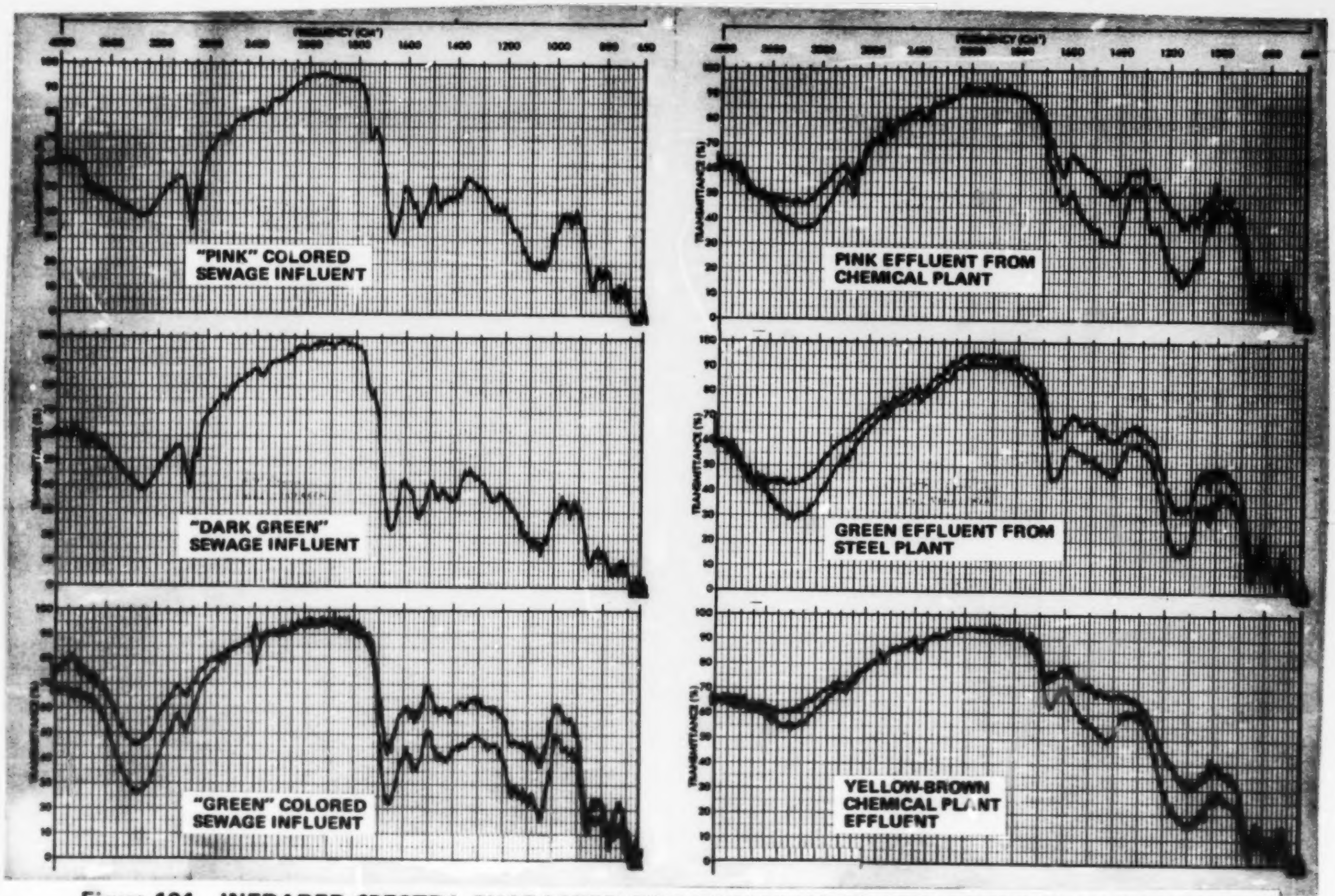


Figure 104 INFRARED SPECTRA CHARACTERIZING TROUBLESOME "COLORED" INFLUENTS TO THE SEWAGE TREATMENT PLANT AND "COLORED" INDUSTRIAL EFFLUENTS BEING DISCHARGED OVER THE SAME TIME PERIOD (JUNE-JULY 1970)

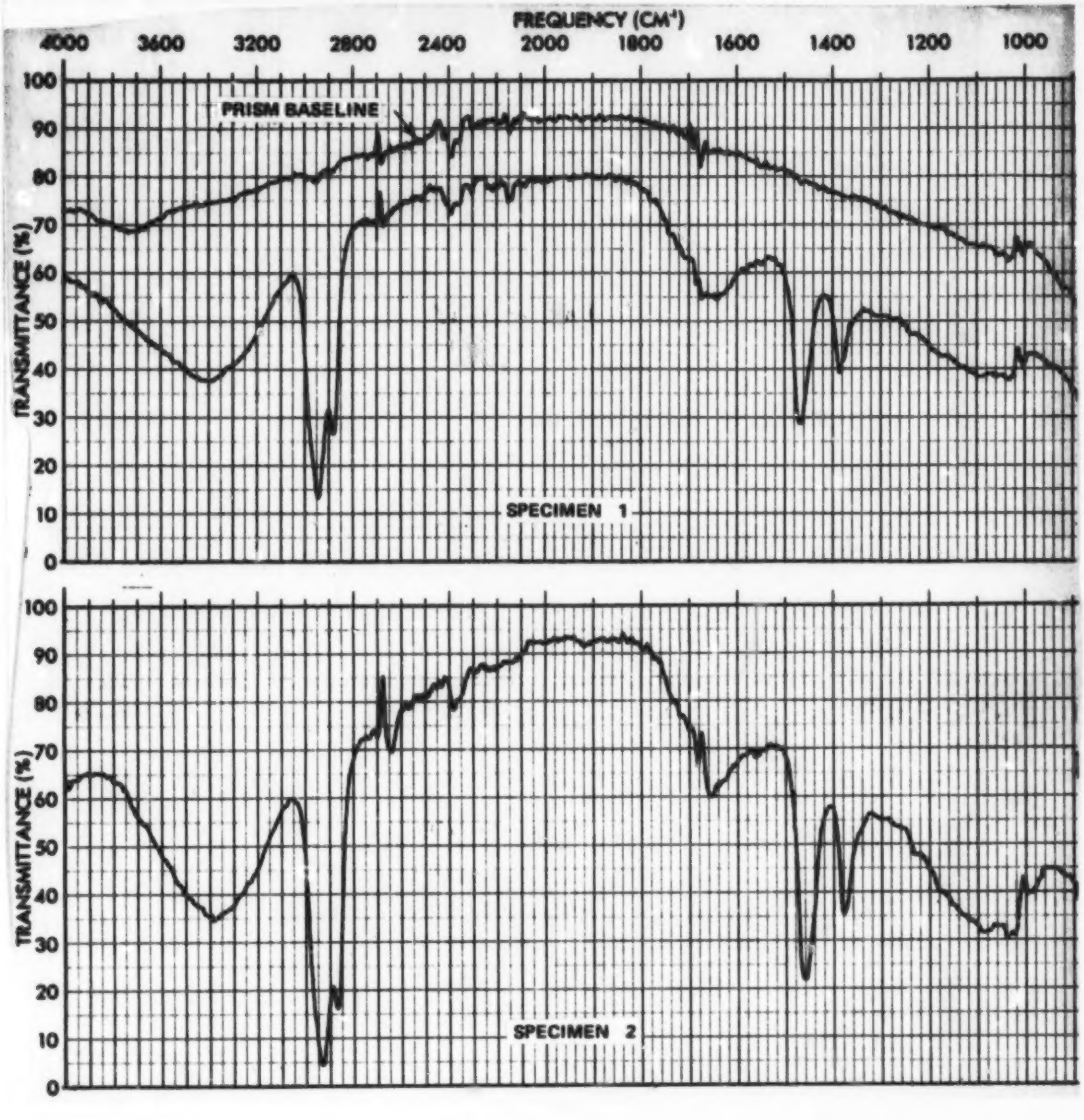


Figure 105 PRELIMINARY INFRARED SPECTRA SHOWING THE ESSENTIAL IDENTITY OF SEVEN SPECIMENS FROM WASTE OIL STORAGE LAGOONS AND FROM THE RIVER SURFACE, AS COLLECTED BY FWQO DURING THE OIL SPILL INCIDENT ON THE SCHUYLKILL RIVER IN NOVEMBER 1970 (SHEET 1 OF 4)

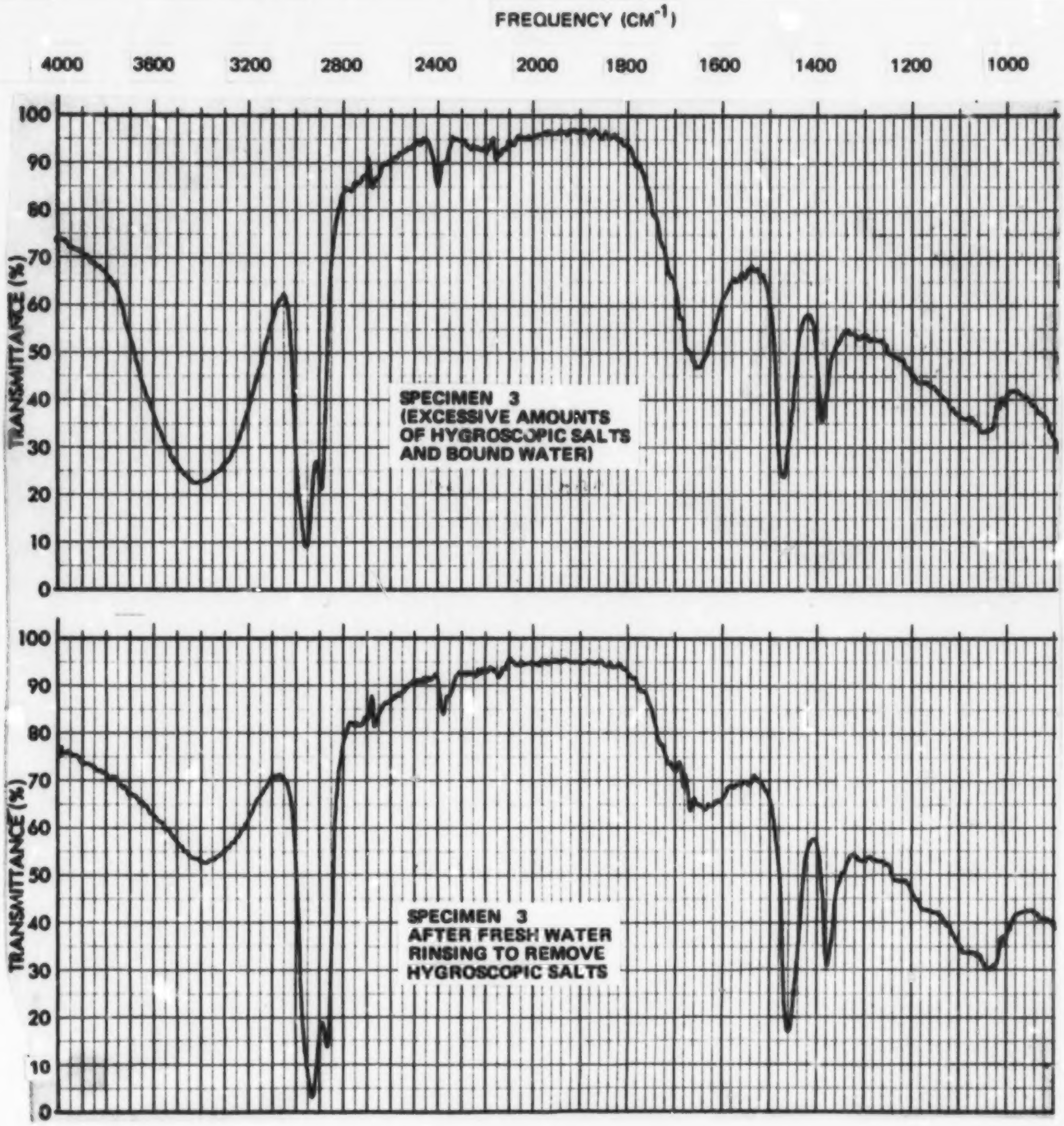


Figure 105 PRELIMINARY INFRARED SPECTRA SHOWING THE ESSENTIAL IDENTITY OF SEVEN SPECIMENS FROM WASTE OIL STORAGE LAGOONS AND FROM THE RIVER SURFACE, AS COLLECTED BY FWQO DURING THE OIL SPILL INCIDENT ON THE SCHUYLKILL RIVER IN NOVEMBER 1970 (SHEET 2 OF 4)

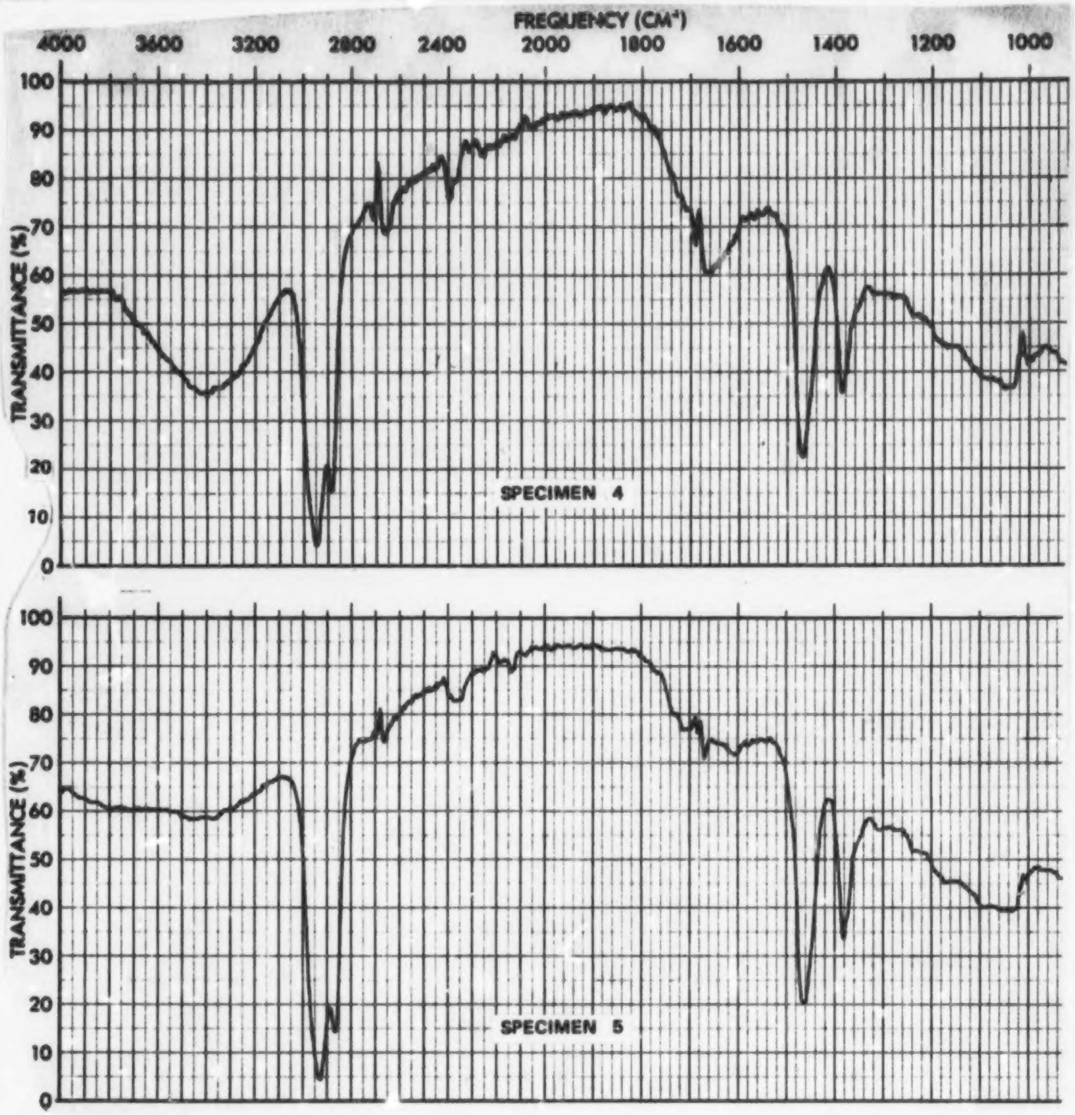


Figure 105 PRELIMINARY INFRARED SPECTRA SHOWING THE ESSENTIAL IDENTITY OF SEVEN SPECIMENS FROM WASTE OIL STORAGE LAGOONS AND FROM THE RIVER SURFACE, AS COLLECTED BY FWQO DURING THE OIL SPILL INCIDENT ON THE SCHUYLKILL RIVER IN NOVEMBER 1970 (SHEET 3 OF 4)

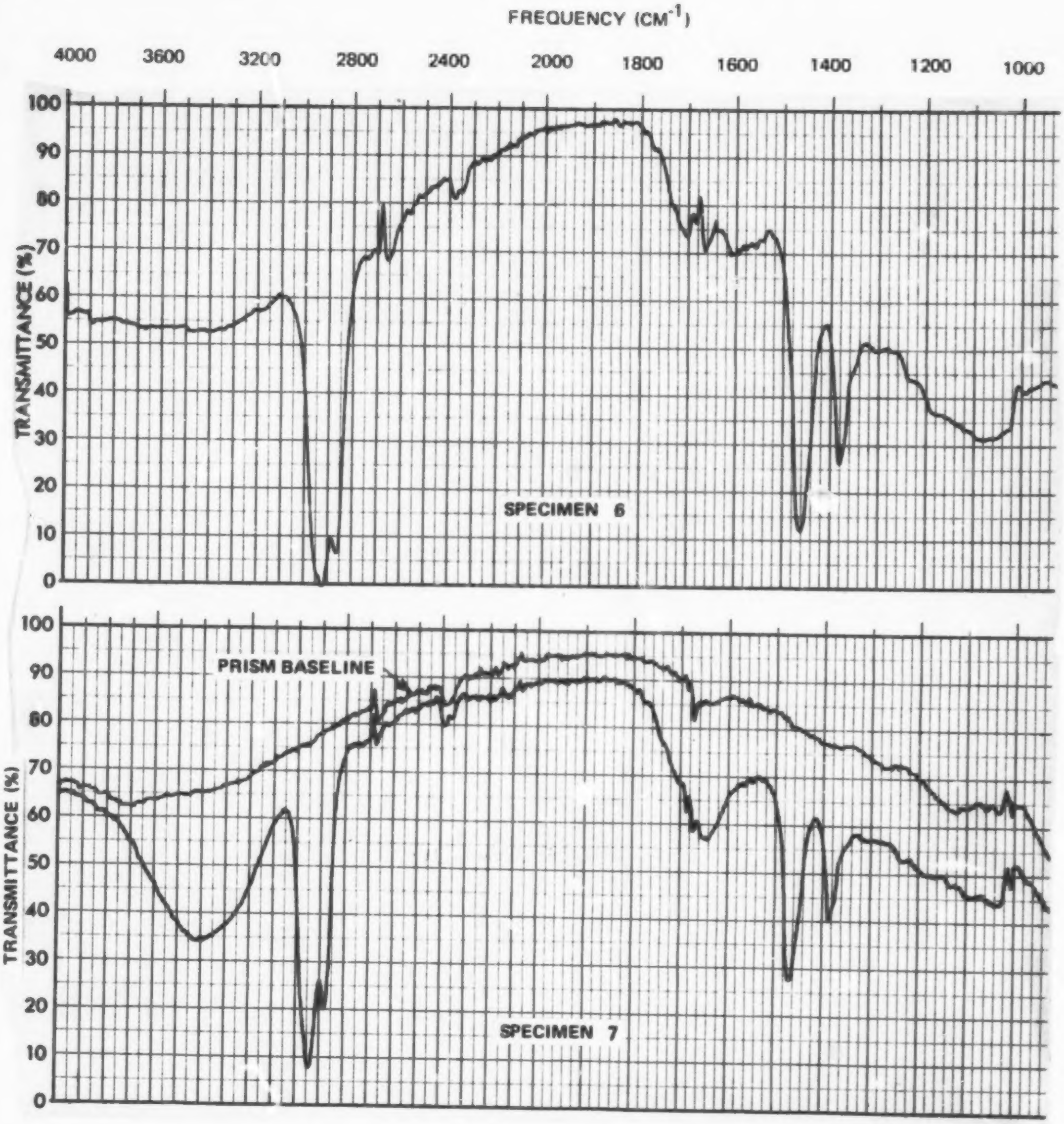


Figure 105 PRELIMINARY INFRARED SPECTRA SHOWING THE ESSENTIAL IDENTITY OF SEVEN SPECIMENS FROM WASTE OIL STORAGE LAGOONS AND FROM THE RIVER SURFACE, AS COLLECTED BY FWQO DURING THE OIL SPILL INCIDENT ON THE SCHUYLKILL RIVER IN NOVEMBER 1970 (SHEET 4 OF 4)

spectral trace at the top of the figure shows the prism baseline for the infrared internal reflection prism used for all of the sample analyses. The final set of traces in that figure shows the prism baseline again, recorded at the end of such analyses, so that shifts in the baseline with continued use and addition of new samples can be estimated.

These preliminary infrared spectra were the first analytical data available in immediate response to the need for identification of oil samples in the waste oil lagoons and from the gross oil slicks floating on the Schuykill River itself. The samples were hand delivered to a Cornell Aeronautical Laboratory representative during one of frequent visits to the Edison, New Jersey laboratories for purposes of consultation on the Buffalo River program.

CASE NO. 5: PRELIMINARY ANALYSES OF A TURBID MUNICIPAL WATER SUPPLY

As a final illustrative case, Figure 106 presents infrared spectra which assisted in identification of the contamination in a municipal water storage tank. The water, as delivered by a local official of a suburb of Buffalo, had been noted to be very turbid by workers who had used it to fill a large pool. The water had been taken from a standard, apparently uncontaminated storage vessel or storage line. The suspicion was that it might have had some oily materials admixed with it or some contaminants of other origin. Figure 106 shows the spectral baseline in the topmost trace. A spectrum from a dried aliquot of the suspected contaminated water is given in the second trace from the top and a spectrum of this same dried aliquot of the municipal water after its rinsing with distilled water (to remove the soluble salts, some of which also have infrared adsorption bands at some of the regions of interest) is given next. Finally, Figure 106 contains an infrared trace from an aliquot of solution of a known polymeric exudate produced by bacterial action. It will be noted in the final two traces in Figure 106 that, although the peaks are not quantitatively the same, qualitatively they are accounted for very well. It will also be noted that the contribution in all these spectra from hydrocarbons, as indicated in the absorption band at 2900 cm^{-1}, is very small. Thus, these spectra eliminated the suggestion that there was some oily contamination of the waters, but did confirm that some contamination was present and that the contamination was most likely of a microbiological origin. The suggestion was confirmed when simple filtering and chlorination of the water eliminated the turbidity permanently.

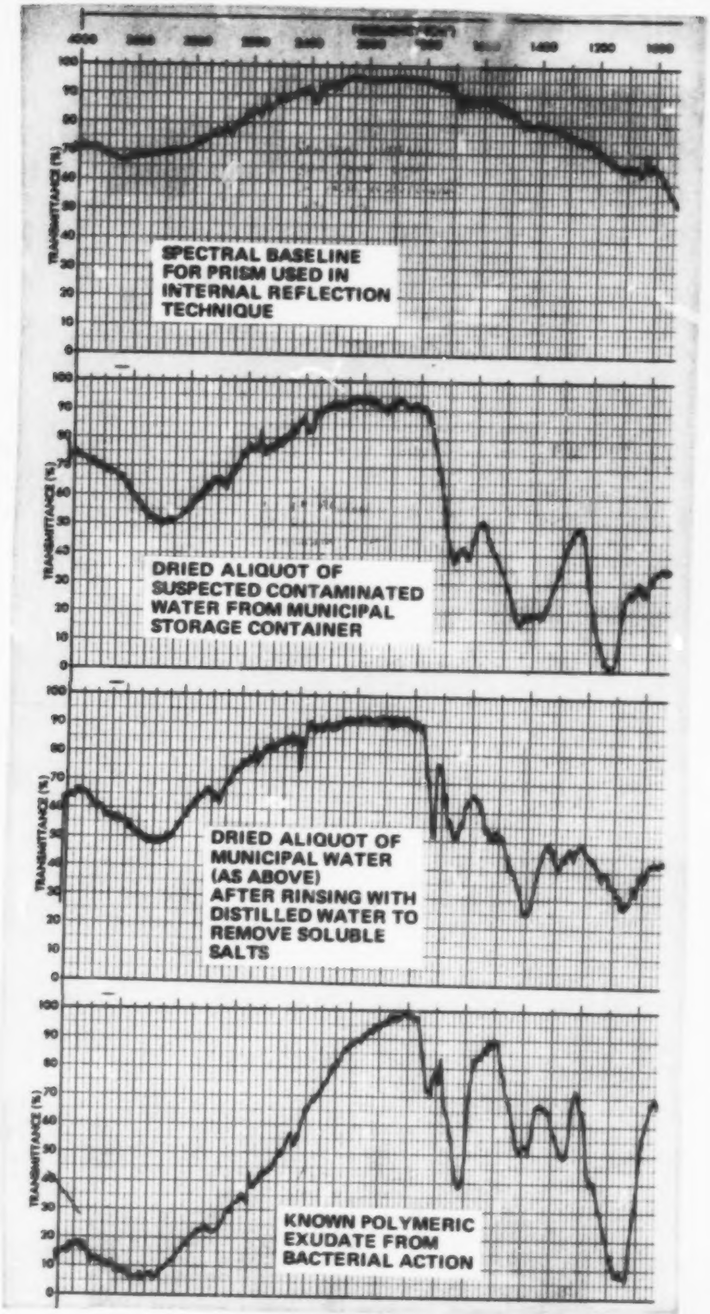


Figure 106 INFRARED SPECTRA WHICH ASSISTED IN IDENTIFICATION OF CONTAMINATION IN MUNICIPAL WATER STORAGE AS OF MICROBIOLOGICAL ORIGIN

APPENDIX A

DETAILS OF THE PRISM DIP TECHNIQUE FOR OIL SAMPLING AND IDENTIFICATION: CALIBRATION AND PROSPECTS FOR DEVELOPMENT OF A DISPOSABLE "ENVIRONMENTAL QUALITY SAMPLING KIT" AND A BUOY-MOUNTED "OIL SLICK MONITOR" BASED UPON THIS TECHNOLOGY

To quantify the results of the prism dip technique, as described in the sampling section of this report and used to good advantage throughout all other tasks addressed herein, calibration charts were prepared to allow reliable estimation of film thickness. For oil slicks in the region from 0 to 1000 Angstrom units, a sample calibration chart (given as Figure A-1) was prepared by running 25 superimposed infrared scans of an internal reflection prism coated with multiple layers of a model polar hydrocarbon compound, stearic acid. The prism was coated in exactly the same manner as during field collection of oil slick samples. The prism dip technique almost quantitatively transfers the oil layer, no matter how thin, to the internal reflection prism surface. When the coated prism is subsequently analyzed by the infrared spectroscopic method known as internal reflection spectroscopy, a spectrum is produced which is directly decipherable in terms of the actual chemical content in the collected film. In the case of oil slicks, the strongest and most diagnostic infrared absorption band is for hydrocarbons in the frequency range from 2950 to 2850 cm^{-1}. As the oil thickness increases from no film at all to a film approximately 1/10 micron thick, the strength of this diagnostic absorption band is seen to increase proportionately but not linearly. Application of our monolayer technology has allowed this increased absorption to be correlated with actual film thickness by producing data for calibration films of known increasing thicknesses in very small increments of only 5/1000ths of a micron.

The plot of such calibration data, as in Figure A-2, allows an immediate and direct estimate of the oil thickness of the slicks recovered from various field sites. For example, if the infrared spectrum recorded by the internal reflection method (from a prism dipped in and out of a polluted water surface) shows a minimal transmittance (corresponding to a maximum energy absorption in the diagnostic hydrocarbon band) of about 50% of the incident radiant energy, then the calibration chart reveals the film thickness to be equivalent to about 250 Angstroms of the calibration film material. For the prism materials used throughout this program, constructed of the semi-conductor, germanium, this useful correlation could not be carried beyond film thicknesses of about 1/10 micron because of depth-of-penetration limitations of the very high refractive index germanium crystal material. As demonstrated in the following paragraphs, other internal reflection prism materials do have considerably greater depths of penetration and make the prognosis for extending the method to thicker films excellent. The range of minimal thickness from about 0 to about

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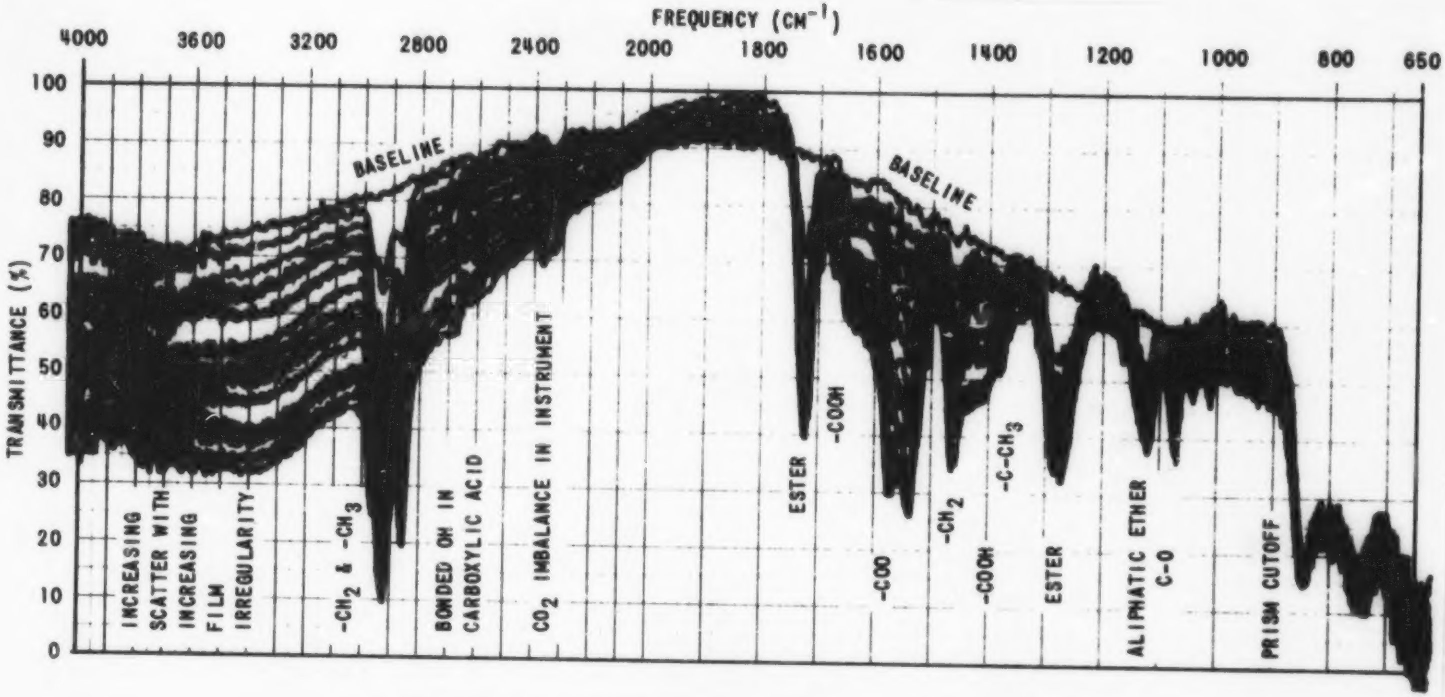


25 SUPERPOSED MAIR INFRARED SCANS OF CLOSE PACKED STEARIC ACID FILMS, REPRESENTING THICKNESSES OF 0 TO 1200 Å AT 48 Å INTERVALS.

FILMS TRANSFERRED FROM THE AIR/WATER INTERFACE BY THE LANGMUIR-BLODGETT TECHNIQUE AT A PACKING PRESSURE OF 30 DYNES/CM.

Figure A-1 CALIBRATION CHART FOR QUANTITATIVE ESTIMATE OF OIL FILM THICKNESS

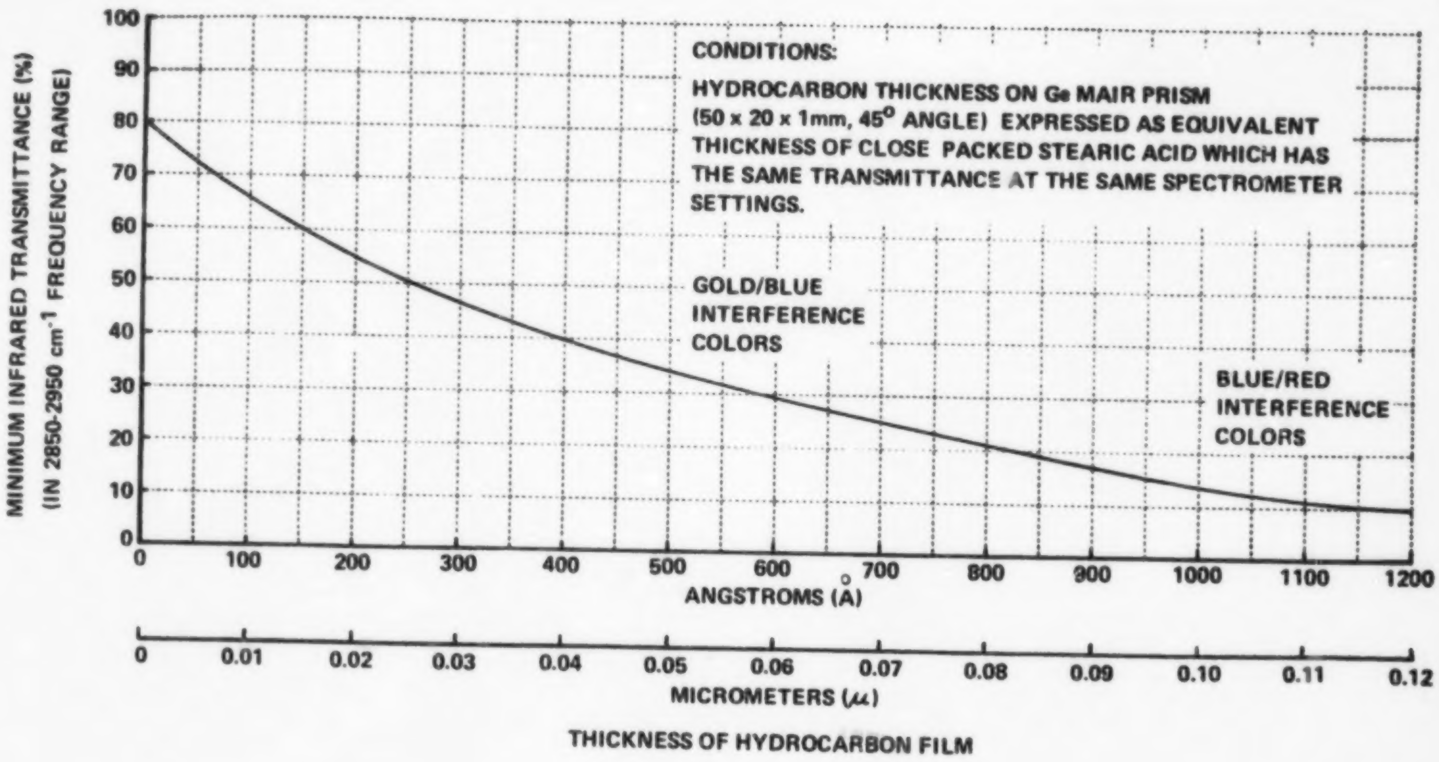
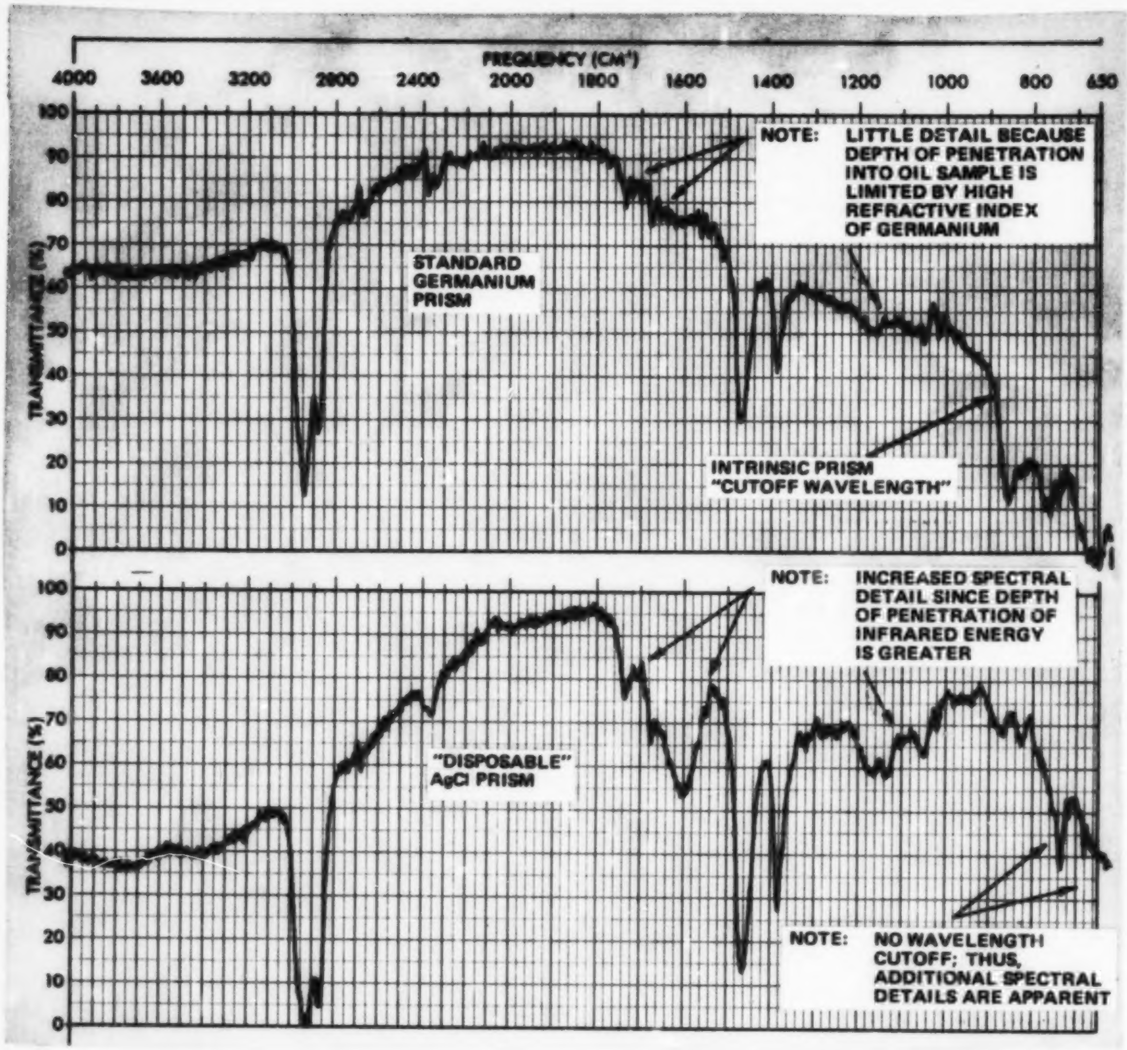


Figure A-2 DATA FOR ESTIMATING OIL FILM THICKNESS FROM IR TRANSMITTANCE a tenth micron is the most frequently encountered film thickness in polluted waterways, however. It is this thickness which goes undetected at present by all other tested methods of field collection and analysis.

Figure A-3 shows infrared spectra of the identical sample of used automotive engine oil on internal reflection prisms constructed of two different infrared-transparent materials. In the upper trace in Figure A-3 is shown the spectrum obtained when the oil was coated onto a standard germanium prism. Deficiencies noted in that trace are the intrinsic prism cut-off wavelength, at about 900 cm^{-1}, and the lack of detail in the diagnostic regions for carbonyl groups and for aromatic groups because of the depth of penetration limitations of the high refractive index germanium. The bottom trace in Figure A-3 shows the infrared spectrum obtained for the identical material as coated onto a potentially disposable prism of much less expensive material, silver chloride. It should be noted here that silver bromide has similar properties to silver chloride. Both of these salts are extraordinarily water insoluble and can be hot pressed or molded in quantity at low cost. The annotations on the bottom trace, in Figure A-3, show the benefits to be gained when silver chloride is used as a prism material for this technique. These benefits are (1) no wave length cut-off is apparent, so that additional spectral details can be recorded at the low wave length end of the spectrum and (2) increased complexity of the spectral signature is apparent in regions of low absorption intensity (as judged from comparison with the germanium prism spectrum above) as a result of the greater depth of penetration of the infrared energy from this lower refractive index material. It is obvious from a comparison of these two spectra that the lower cost, disposable material is also superior in providing spectral detail of environmental pollutants; and, in this example, specifically oil films on water

Figure A-4 presents a sequence of spectra illustrating the general utility of silver chloride prisms for sampling of both thin and thick oil films. This sequence of spectra also shows the unfortunate deterioration of prism spectral baseline with repeated cleaning of oil films from the surface. This is a failing with the softer, internal reflection materials. The general reason that materials like germanium, silicon, and sapphire have most often been selected as standards for the analytical laboratory is that these materials can be solvent or detergent-cleaned of pollutant films repetitively without significant degradation of their spectral baselines. The spectra collected in Figure A-4 show the sensitivity of the silver chloride internal reflection prisms to the presence of a very thin layer of oil and to a very thick layer of oil, and also show the changes in baseline which were encountered during routine cleaning of these prisms between experiments.

In an experimental series using silver bromide prisms, which are still considered experimental materials and not direct replacements for silver chloride, a similar sensitivity of the prism baseline to roughening of the surface by routine cleaning was observed. However, in calibration experiments using both the silver bromide prisms and



NOTE: LITTLE DETAIL BECAUSE DEPTH OF PENETRATION INTO OIL SAMPLE IS LIMITED BY HIGH REFRACTIVE INDEX OF GERMANIUM

INTRINSIC PRISM "CUTOFF WAVELENGTH"

NOTE: INCREASED SPECTRAL DETAIL SINCE DEPTH OF PENETRATION OF INFRARED ENERGY IS GREATER

NOTE: NO WAVELENGTH CUTOFF; THUS, ADDITIONAL SPECTRAL DETAILS ARE APPARENT

TOP: STANDARD GERMANIUM PRISM

(NOTE: STANDARD SILICON PRISMS HAVE EVEN LOWER WAVELENGTH "CUTOFFS"; STANDARD KRS-5 PRISMS ARE ETCHED BY CONTACT WITH WATER AND RENDERED INFRARED-OPAQUE)

BOTTOM: PROPOSED "DISPOSABLE" PRISM OF AgCl

(NOTE: AgBr HAS SIMILAR PROPERTIES; BOTH ARE ESSENTIALLY WATER INSOLUBLE AND CAN BE HOT PRESSED OR MOLDED IN QUANTITY AT LOW COST)

IT IS OBVIOUS FROM THESE SPECTRA THAT THE LOWER COST, DISPOSABLE MATERIAL IS ALSO SUPERIOR IN PROVIDING SPECTRAL DETAIL OF ENVIRONMENTAL POLLUTANTS (e.g. OIL FILMS ON WATER)

Figure A-3 INFRARED SPECTRA OF THE IDENTICAL SAMPLE OF USED AUTOMOTIVE ENGINE OIL ON INTERNAL REFLECTION PRISMS CONSTRUCTED OF TWO DIFFERENT INFRARED-TRANSPARENT MATERIALS

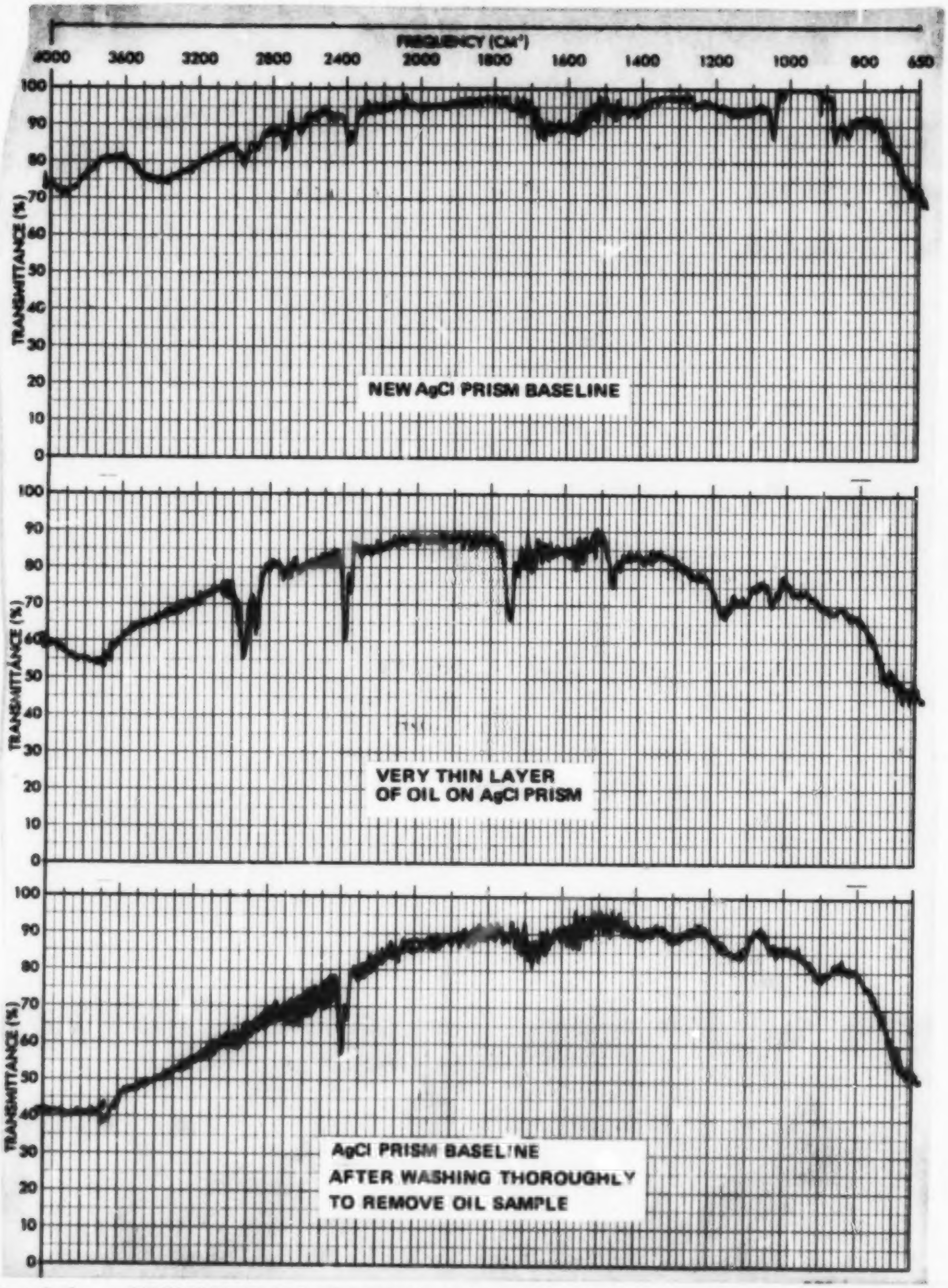
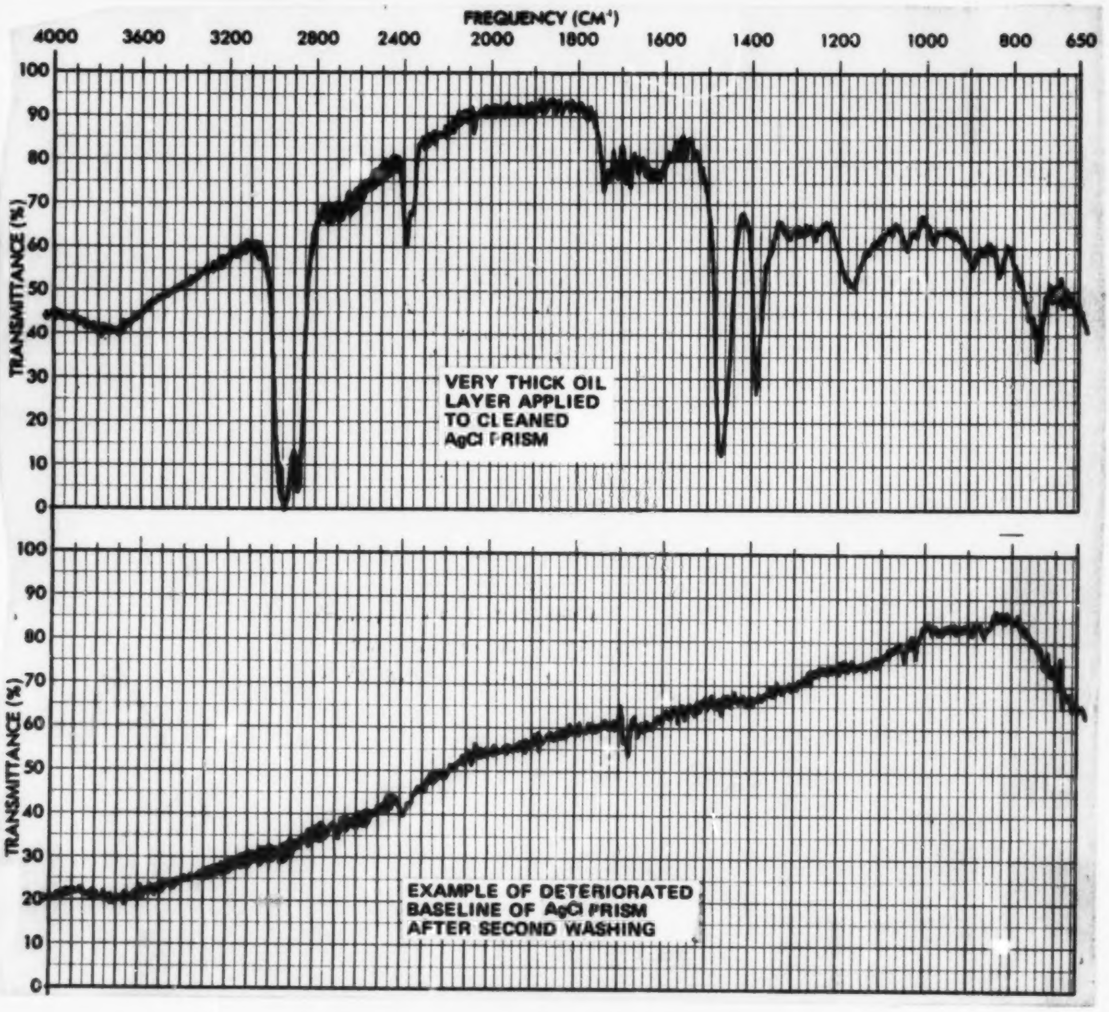


Figure A-4 SEQUENCE OF SPECTRA SHOWING UTILITY OF AgCl PRISMS FOR SAMPLING OF THIN AND THICK OIL FILMS, AND SHOWING DETERIORATION OF PRISM SPECTRAL BASELINE WITH REPEATED CLEANING (SHEET 1 OF 2)

NOTE: GERMANIUM PRISMS CAN BE SOLVENT- OR DETERGENT-CLEANED OF OIL FILMS REPETITIVELY WITHOUT SIGNIFICANT DEGRADATION OF SPECTRAL BASELINE, WHEREAS THE SOFTER SALT (AgCl) PRISMS SHOW BASELINE VARIANCE



VERY THICK OIL LAYER APPLIED TO CLEANED AgCl PRISM

EXAMPLE OF DETERIORATED BASELINE OF AgCl PRISM AFTER SECOND WASHING

Figure A-4 SEQUENCE OF SPECTRA SHOWING UTILITY OF AgCl PRISMS FOR SAMPLING OF THIN AND THICK OIL FILMS, AND SHOWING DETERIORATION OF PRISM SPECTRAL BASELINE WITH REPEATED CLEANING (SHEET 2 OF 2) silver chloride prisms it was seen that oil pollutant films, as thin as single monomolecular layers (that is, with thicknesses of the range of 20 to 30 Angstrom units) could readily be detected. In the infrared scans of silver salt prisms coated with film thicknesses of 75 Angstroms, of 125 Angstroms, and of 175 Angstroms, one noted increasing degrees of attenuation of the infrared energy in the region of hydrocarbon absorption near 2900 cm^{-1}. It is known that new accessories in standard infrared spectrophotometers allow further miniaturization of the internal reflection prisms without great sacrifice in their sensitivity. Taking into account the significant advantages that the silver salts present in terms of their initial lower cost and their ease of automated fabrication, we consider the prognosis excellent for the creation of a disposable, pre-packaged kit for environmental quality sampling using internal reflection prisms.

Figure A-5 is a schematic embodying the concept just described. We envision the eventual use of such pre-packaged disposable kits by enforcement and monitoring personnel of Federal, State and Regional agencies. Independent laboratories would provide, at the same time, a service whereby such kits can be used as follows: At the site of a suspected oil spill, a suspicious oil slick on the water surface, or suspicious industrial outfall, the investigator would simply pull the prism (in its plastic holder) from a sheath-like container, dip it once in and out of the water surface or any other suspected pollutant material, be it solid or liquid, replace the prism "dagger" in its "sheath," and mail the unit in a pre-paid mailing envelope very much like that provided with photographic film, to a nearby central laboratory. There, the infrared spectral scan would be recorded and annotated by a skilled technician and returned in the original mailing envelope to the investigator for his disposition. The prism would be marked as to its source and arrival date and kept on file as a permanent exhibit in the analytical laboratory.

The need is also great for the development of a continuous monitor for the surface quality of industrial watercourses, sanitary sewer lines where oil spills are frequent, and in the vicinity of oil drilling operations such as in the Gulf of Mexico or the Santa Barbara Channel. Internal reflection spectroscopy has been demonstrated here to be far superior to transmission spectroscopy in its inexpense and rapidity of fielding. It can also provide an effective answer to the need for detecting and identifying the presence of oil slicks in real time. The use of such prisms in a buoy-mounted design, described briefly in the following paragraphs, is superior to concepts for remote monitors which do not require any physical contact with the water or the oil slick, since all such remote methods are subject to triggering by "false alarms" and to ambiguities in the interpretation of their signals. The internal reflection technique, in the field, would catch all adventitious spills and, at times inconvenient to the presence of a human monitor or inspector, could record this information permanently on a chart read-out both as to time of the spill and intensity of it. In addition, the capability exists for an unambiguous identification of

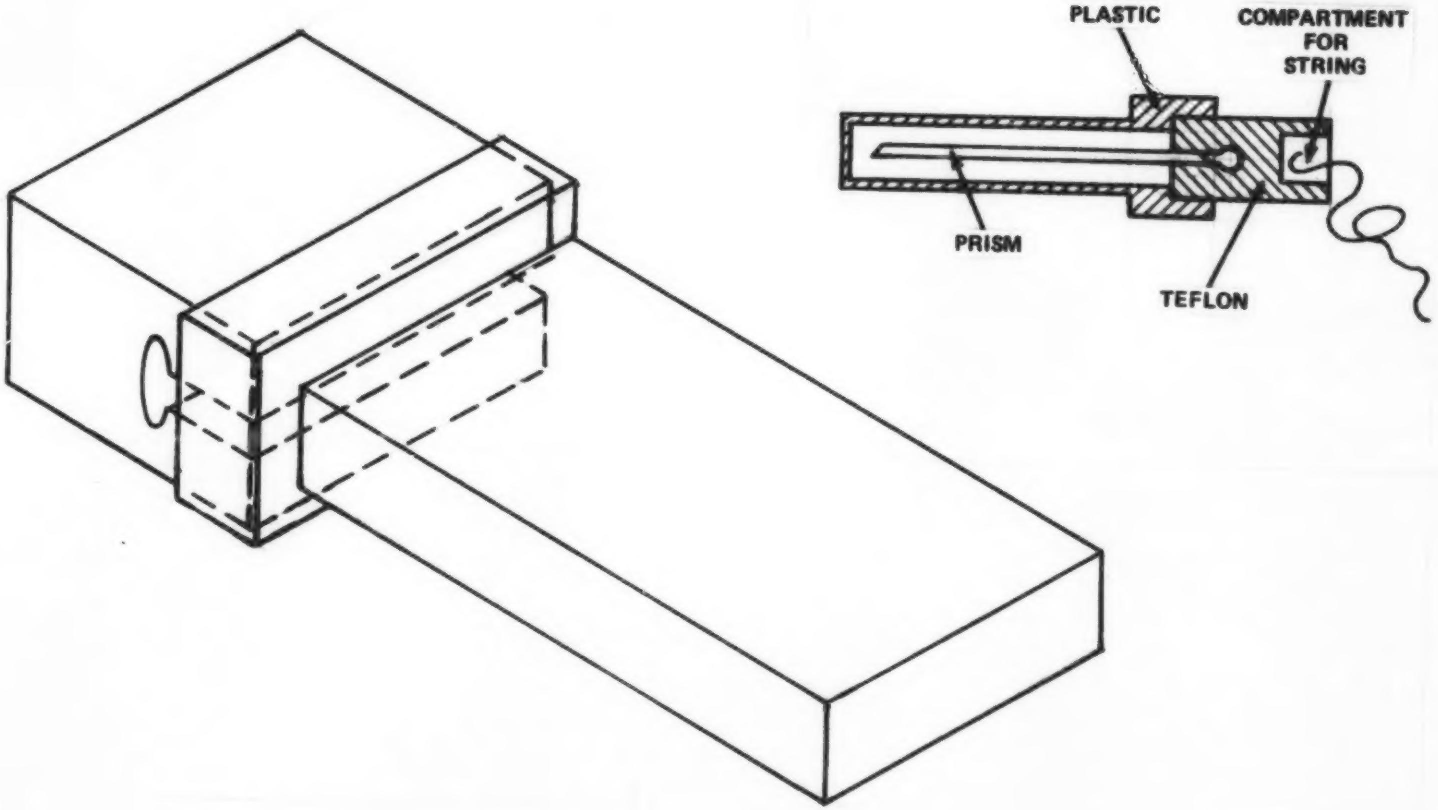

PLASTIC
COMPARTMENT FOR STRING
PRISM
TEFLON

Figure A-5 DISPOSABLE PREPACKAGED KIT FOR ENVIRONMENTAL QUALITY SAMPLING USING INTERNAL REFLECTION PRISMS the slick material because a large infrared region for "fingerprinting" pollutant films is available for continuous recording as well. In a buoy-mounted, internal reflection probe, the probe can be kept stationary, at a given depth with respect to the water surface, and the detection made of the proportion of the probe surface which is oil covered. This potential design will most likely be made valueless in very choppy water states where the water and the oil-covered water films will lap up and down over the infrared probe and will constantly change the reading of the amount of oil present. Thus, our preferred embodiment of this concept includes a dip mechanism where every so often an internal reflection prism is lowered through the air/water interface and then retracted again into a closed device and the signal read. There is already a prototype device manufactured by the Wilks Scientific Corporation of South Norwalk, Connecticut which is an advanced unit capable of being field operated and of automatically scanning the entire infrared range. It is also capable of maintaining its surveillance at a fixed wavelength (for example, the fixed wavelength typical of the hydrocarbon bands and oil films). We expect that this less expensive modification of the device will be the first to be fielded.

In our preliminary experiments with the device at the Wilks Scientific Corporation, it was learned that each ambient oil thickness has its own specific maximum attenuation of the infrared energy transmitted through the internal reflection probe. This correlation extends to film thicknesses much beyond the thicknesses to be expected on the basis of the most simple depth-of-penetration calculations from internal reflection spectroscopic theory. However, the more complete and detailed theoretical treatment which accounts for back-reflections and secondary refractions of the infrared energy within the thicker films is consistent with our observation that different oil thicknesses can be assessed directly on a dipping probe device.

As far as creating or engineering the field mount for such a monitoring device, similar instrumentation has already been successfully designed, developed, calibrated and installed for recording various parameters at several points in natural bodies of water. In a study at Cayuga Lake, for example, Cornell Aeronautical Laboratory constructed four buoys which were connected to the shore by coaxial cable. The measured water data were transmitted over the cable by audiotones which were frequency modulated by the variable being measured. The cable also carried power for the operation of the buoy-mounted instruments and for the low-frequency command signals of the various sampling instruments at each buoy. Time division multiplex was used for sampling of up to 24 signals from each of the buoys and to permit transmission of the signal via the single coaxial cable. At the shore, the data were extracted and recorded in digital or analog format. The output of a digital-to-analog converter deflected a paper chart recorder pen, for monitoring purposes. Such readily sampled signals could be transmitted over a telephone voice quality line to permit remote access to the data which was a useful feature for equipment maintenance and is suggested for installation in a buoy-mounted internal reflection probe as well.

Since all natural bodies of water are likely to be, from time to time, the sites of casual or industrial boating, where outsiders will have easy access to the buoys, it is necessary that they be designed so that they are quite difficult to damage. In the buoys already successfully designed for previous Cornell Aeronautical Laboratory programs, a truncated cone shape was adopted for both the top and bottom portions to assure hydrodynamic stability. To further enhance stability and provide for connections between the instruments and the cables, a central hatch was formed into the bottom portion. It is this central hatch in which we envision the insertion of a field oil-slick monitoring device such as that now commercially available from the Wilks Scientific Corporation (using internal reflection spectroscopy).

Because of the symmetry of this design, the pitching frequency of the buoys equals the rolling frequency and is about 0.2 hertz. The heaving resonance is approximately 1.6 hertz. With these features of stability, the buoys proved quite stable under the wave conditions, which were occasionally quite severe, encountered at Cayuga Lake in central New York State.

For more distant locations where cable attachment of the buoys to shoreline monitoring stations is not likely to be reliable, a telemetry system is suggested. One particular telemetry system, with which we have experience, consists of a timing generator which applies power to a 26.995 megahertz transmitter once every sampling period for about 20 seconds. During the sampling interval, the DC currents from the sensor (which range from 0 to 1 milliamp) are sampled and passed through gates to a voltage controlled oscillator. The voltage controlled oscillator then generates a note of 500 hertz to indicate the start of transmission of the data followed by a series of variable frequency notes which could indicate, in the internal reflection technique, whether the prism probe had encountered oil (in which case a frequency of 1 kilohertz will be broadcast) or water alone (in which case a signal of 2 kilohertz will be broadcast). According to the thickness of the oil pollutant collected, and, therefore, according to the degree of attenuation of the infrared wave length transmitted and monitored, a full range of intermediate frequencies would be broadcast. The notes thus broadcast would modulate the transmitter and, at the remote field station or office station, the receiver and an FM demodulator can convert the tones back to voltages that are displayed on a paper chart recorder. In the current studies with such a telemetry system for transmitting data from sewer lines, the 500 hertz tone that indicates the start of transmission is also used to start the chart drive so as to keep the records compact.

A potential problem with the buoy-mounted internal reflection probes for monitoring oil film presence and thickness is the difficulty of maintenance of the suggested unit. The major difficulty in such maintenance will be the potential permanent fouling of the internal reflection prisms themselves with debris or with weathered oil slicks.

To overcome this potential difficulty, it was desirable to experiment briefly with a coating of the prism elements with non-interfering films that would shed both water and oils after a given period of time. Very low surface energy fluorocarbon coatings are theoretically best suited for this purpose. Figure A-6 shows infrared spectra illustrating the promising prospects of precoating internal reflection prisms with such a hydrophobic and oleophobic layer to improve its cleanability. There is the clear likelihood of routine prism reuse by either spontaneous draining of the oil from the low energy surface with time between sampling instances or by assisting the removal of oil films and debris with an occasional jet of cleansing water or solvent stored in the buoy itself.

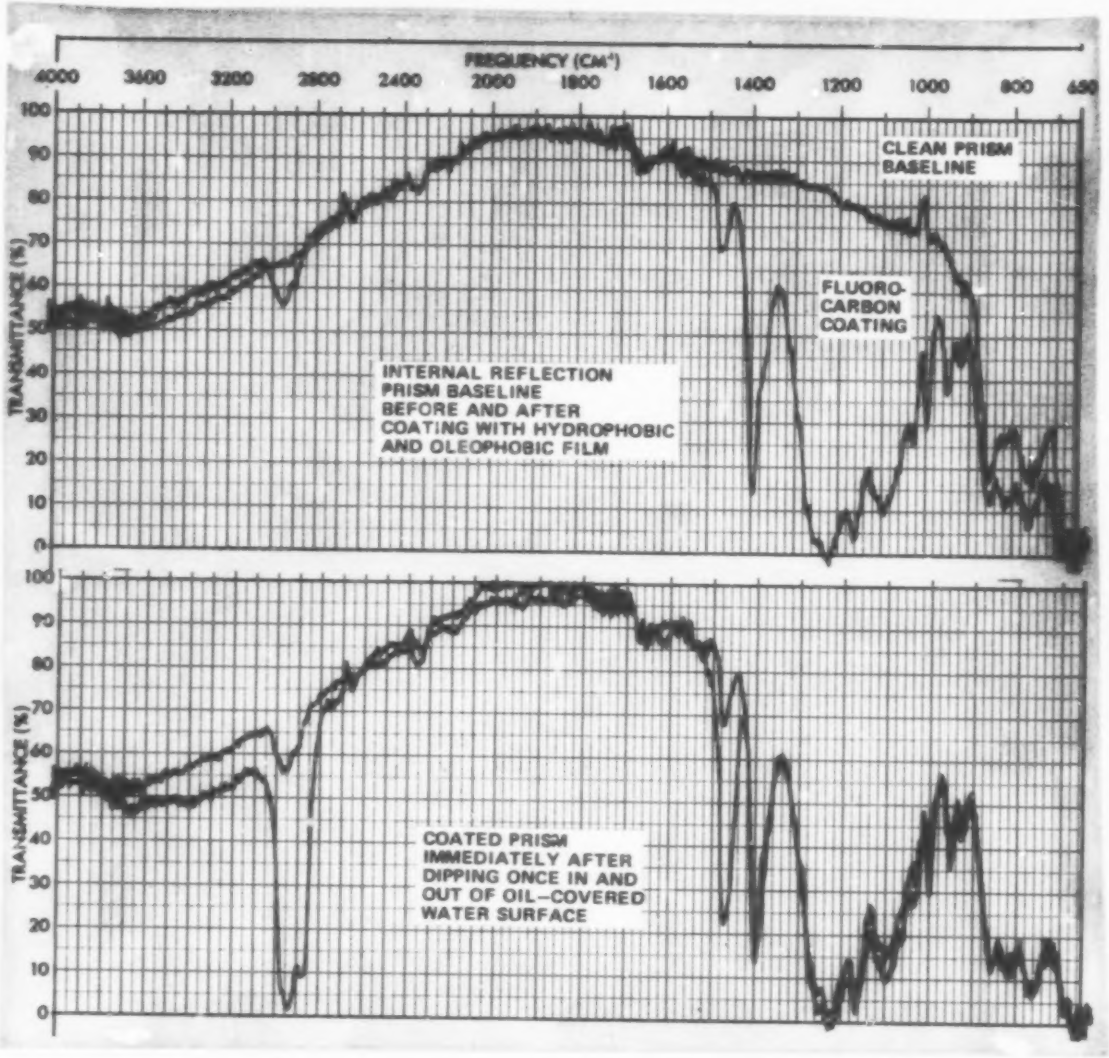


Figure A-6 INFRARED SPECTRA ILLUSTRATING THE PROMISING PROSPECTS OF PRECOATING THE INTERNAL REFLECTION PRISMS WITH A HYDROPHOBIC AND OLEOPHOBIC LAYER TO IMPROVE "CLEANABILITY" AND PRISM REUSE

APPENDIX B

THE ANALYTICAL CHEMICAL TECHNIQUE SELECTED FOR ROUTINE USE IN THE ANALYSIS OF OIL IN BUFFALO RIVER SAMPLES

CHLOROFORM EXTRACTABLE MATERIALS IN BUFFALO RIVER WATER

This technique is applicable to determining the ppm level of chloroform-soluble pollutants in water and industrial waste (water). It is a modification of the standard method of the American Society for Testing and Materials, designated as ASTM: D1178-60 (defined by Stepwise Procedure below).

I. Secure a sample of 800-1000 ml.

II. Measure pH with suitable equipment. Record pH.

III. Acidify sample to pH 3-4.

IV. Transfer sample to suitable separatory funnel.

V. Extract 3 times with chloroform: one 50 ml and two 20 ml portions.

VI. Collect all chloroform portions in a tared vessel (glass beaker). Vessel weight should be measurable to ±50 μg.

VII. Drive off almost all chloroform on heat source not to exceed 50-60°C. Finish desolvation at temperature not to exceed 40°C. Allow vessel to come to thermal equilibrium.

VIII. Weigh vessel containing residue periodically until constant weight is achieved.

IX. Calculate concentration of pollutants extracted:

$$\text{ppm} = \frac{(W_S - W_T)}{S} (10^6)$$

where: W_S = weight in grams of vessel plus residue
W_T = tare weight of vessel in grams
S = weight in grams of sample used (to nearest gram)

This procedure differs somewhat from ASTM 1178-60. It is simpler in that it requires fewer transfer steps.

CHLOROFORM EXTRACTABLE MATERIALS IN INDUSTRIAL EFFLUENTS

The analysis of samples from industrial outfalls for chloroform-soluble material is identical to that for other water samples except that the acidification step is omitted. The pH is, nevertheless, to be recorded. The samples are not acidified for fear of altering solubility of materials that may be pH sensitive.

Follow the same stepwise procedure as given above.

CHLOROFORM EXTRACTABLE MATERIALS IN MUD AND SEDIMENT SAMPLES

Mud and sediment samples are analyzed differently. Several hundred grams of mud sample are stirred to achieve homogeneity. The following is a stepwise procedure for the estimation of adsorbed or entrapped oils:

I. Weigh to nearest 0.1 gm about 10 gm of homogenized mud.

II. Wash sample into blender (e.g., a Waring Blender) with 100 ml distilled water.

III. Add 50 ml chloroform. Agitate at low speed for 5 minutes.

IV. Filter resultant slurry through No. 31 Whatman paper in Buchner funnel.

V. Wash filter cake three times with 50 ml portions fresh chloroform.

VI. Transfer filtrate to suitable separatory funnel, rinsing filter flask with more fresh chloroform. Separate chloroform layer into a tared vessel (weighed to ±50 μg).

VII. Drive off most of the chloroform using a heat source not to exceed 50-60°C. Finish desolvation at temperature not to exceed 40°C.

VIII. After vessel has come back to thermal equilibrium, weigh periodically until constant weight is achieved.

IX. Calculate % chloroform extractable material as follows:

$$\% = \frac{(W_S - W_T)}{S} \; 100$$

where: W_S = weight in grams of vessel plus residue
W_T = tare weight of vessel in grams
S = weight in grams of initial sample (to nearest 0.1 gm).

APPENDIX C

COMMENTARY TO ACCOMPANY FILM ON THE USE OF PISTON FILMS TO DISPLACE OIL SLICKS IN AN INDUSTRIAL WATERCOURSE

The film opens with a short segment officially released by the U.S. Navy and provided by technical personnel at the Naval Research Laboratory. It shows the various general types of pollution that exist in our environment, including water pollution, land pollution and air pollution. The scene then shifts to an oil spill on water, which is ignited and burns with emissions of deep, black smoke.

A brief aerial view of the Naval Research Laboratory, in Washington, D.C. is presented, and the scene shifts to an inside laboratory containing a large model pool where an oil displacement experiment is about to take place. Conducting the experiment are Mr. William D. Garrett, Head of the Interface Chemistry Section, Ocean Sciences and Engineering Division of the Naval Research Laboratory, and his co-worker Mr. William Barger. Observers are Dr. J.H. Schulman, Director for Materials Research at the Naval Research Laboratory, Navy Captain J.C. Matheson, military commander in charge of the research facility, and Dr. V.J. Linnenbom, Superintendent of the Ocean Sciences and Engineering Division. Garrett places a single drop of a surface-active agent on a clean water surface supporting a deliberate gross spill of Navl special fuel oil. The film shows that the surface-active agent forms a piston film which rapidly compresses the oil into a thick black puddle at the far end of the pool. These thickened slicks can be easily picked up by any of a number of collection devices. A simple suction device is demonstrated in the film. The water quality after such a surface-active piston film cleaning operation is extraordinarily good. It is left coated with only a monomolecular layer. Although piston films are only about 1/10,000,000 of an inch thick, they can drive away or compress oil of thicknesses up to 1 centimeter and can work advantageously in sea states with waves up to white caps and at wave heights up to 4 or 5 feet. The major disadvantage of the method is that it cannot work against a wind of more than a few knots.

The film then pans the shoreline of the Buffalo River, and shows regions where oil has completely coated the rocks and walls to depths sometimes measured more than an inch thick. The scene then shifts to an adjacent bridge which overlooks the outfall of a major chemical firm. At the time this film was taken, the effluent was being discharged from an underwater pipe and was delivering a copious quantity of oil and foam. This bridge, from which the film was taken, closed for an entire year because of an oil fire which did take place on the Buffalo River surface beneath it in January 1968.

The scene then shifts to the shoreline at the abutment of this bridge, where advantage is taken of a small trickling stream from the overflow of a storm sewer. A few drops of a surface-active agent, sorbitan mono-oleate, are placed in this stream as it flows to the River surface which is completely polluted with a totally-covering oil slick. The movie sequence then shows the rapid initiation of spreading of the surface-active agent and the displacement of oil. The stream velocity gives the spreading agent the additional advantage of a bit of horizontal surface velocity. The surface-active material is very efficient and the few drops applied completely drive the oil from the location as it is being viewed, demonstrating the utility of this approach for keeping natural oil traps free of oil and debris. Similarly, piston films can drive oil from under piers and other inaccessible structures for the purpose of skimming and removal. An additional advantage of compressing, concentrating and thickening oil for its removal by a skimming device or a suction nozzle is apparent.

This scene continues to shift to an overview of a wooden pier which runs directly under the bridge at this location. The cleared area spreads continuously out in a semicircular fashion, driving the oil before it. The edge of the thickening oil mass is quite sharp. The water quality in the region from which the oil has been displaced is as scrupulously clean as any that is encountered in Nature. It is coated only with a monomolecular layer of a food grade organic compound which is biodegradable. The subsurface water quality is not affected.

Next shown is a brief demonstration of the remote application of this surface-active material using a spray gun. The material itself is a bit like honey in its natural form. In order to apply it remotely, it can be cut with a less viscous material. A common commercial fraction of high-boiling alcohol does an excellent job of diluting the material for dispersal and yet does not impair the excellent surface-spreading properties of the agent itself. The film shows that as soon as each surfactant-containing alcohol droplet hits the water surface, it nucleates an area of "cleansing" and spreads rapidly to force the oil and debris away and leave the water surface scrupulously clean.

The scene shifts to the slip of a Buffalo fire boat. There is a brief demonstration of the oil slick in this enclave being completely driven out of the slip and into the main stream of the river where it can be coped with more readily. The oil in this location was especially difficult to remove because it was admixed with and stiffened by grain and biological materials.

The movie then shows the situation where the major limitation of the spreading agent is demonstrated. The surface-active agent is applied along a concrete abutment adjacent to another bridge which crosses the Buffalo River in a location where the wind is onshore. The spreading agent has a great deal of difficulty driving the oil away from that shore as long as the wind is continuing to compress and hold the oil slick in that location. The surface chemicals presently used do not have a large enough margin of spreading pressure to overcome the coupling of the wind to the oil-coated surface. Further development of such compounds is recommended.

The final scene is at a more neutral location with respect to wind direction. The surface-active agent is dispensed with an eye dropper from the center of the same bridge across the Buffalo River just seen. In this case, the wind, although blowing, works neither with nor against the spreading agent. The initially cleared patch grows very rapidly into a large circular area. Half of the cleared circle is invisible in this sequence since it forms underneath the bridge. The compressed oil layer becomes so thick and rigid that it appears to be broken through as if it were a piece of brittle plastic. Wedges appear where the spreading agent continues to move it back towards a confining boom for later collection.

This film can be borrowed by qualified requesters through the Cornell Aeronautical Laboratory, Inc. Library.

ACKNOWLEDGMENTS

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In addition to providing financial support for the program, the Buffalo Sewer Authority was extremely cooperative in making personnel available for assistance on this phase of the program and in providing survey data for the Buffalo River and its cooling water project. Sincere thanks are extended to Mr. Gillman J. Laehy, General Manager of the Buffalo Sewer Authority, and members of his staff -- particularly, Mr. John Kutch, Jr., Principal Engineer; Mr. Earl Broxup, Senior Engineer; Mr. Richard A. Kressin, Associate Chemist; and Mr. Louis Gugliuzza, Chemist, who were responsible for many of the sample analyses performed. Thanks are also due Mr. Sam Pecoraro of the BSA, who assisted on numerous occasions in the extensive collection of sewer samples.

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Three organizations originated techniques or devices which are the bases for some of the approaches used in the work described. The Naval Research Laboratory, Washington, D.C., initiated the use of chemical displacing agents as piston films for controlling the size and motion of oil slicks on water. This technique was used by CAL to concentrate surface oils for collection by skimmers. To ensure that the surface oil so collected would not be replaced by additional oil contained in the water just below its surface, the amount of the latter oil was assessed using a screen sampling technique, also first employed by the Naval Research Laboratory. Because the screen method of sample recovery is laborious and time-consuming, this oil was also sampled semi-automatically by a small rotating drum skimmer based on the device first used by the Scripps Institute of Oceanography. To identify oil films *in situ*, CAL has proposed use of a concept in which an internal reflection prism is periodically and automatically lowered into the air/water/oil interface and then retracted into instrumentation by which the infrared spectrum of the oil film is obtained.

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